

~~METHOD OF REFORMING ELEMENT SURFACE, ELEMENT WITH~~  
~~REFORMED SURFACE, METHOD OF MANUFACTURING ELEMENT WITH~~  
~~REFORMED SURFACE, SURFACE TREATMENT LIQUID FOR~~  
**WITH POLYMER MATERIALS**  
~~FORMING REFORMED SURFACE, AND METHOD OF~~  
5 ~~MANUFACTURING SURFACE TREATMENT LIQUID~~

Background of the invention

Field of the invention

10 The present invention relates to a method of reforming <sup>a</sup> surface of an element <sup>by</sup> ~~for~~ changing ~~its~~ characteristics, properties, or the likes <sup>to provide</sup> desired characteristics and properties <sup>① This method</sup> <sup>② which is</sup> applied to the surface of an element (the inner face, outer face, or both of the element) or the surface of  
15 an element <sup>that</sup> ~~whose surface~~ has been subjected to some treatment, <sup>Also,</sup> and the present invention ~~also~~ relates to any element subjected to the surface reforming treatment.

The present invention especially relates to a surface reforming method, which can be carried out to  
20 reliably reform the surface of an element such as a fiber, a particle, or a container made of an olefinic resin <sup>which is</sup> difficult to ~~be surface treated~~ but <sup>is</sup> harmless to ~~the~~ environments <sup>g</sup>, and relates to a method of manufacturing an element and a fiber having <sup>a</sup> reformed surface.

25 Related Background Art

Conventionally, though the characteristics and the properties of an element are dominated <sup>by</sup> with the

characteristics of <sup>its</sup> the constituent material, a desired characteristic <sup>can be</sup> is provided by reforming the <sup>elements</sup> surface characteristic. The desired characteristic, <sup>are, for example,</sup> sometimes means a reactive group having a reactive property such as <sup>hydrophobic</sup> water-repelling property <sup>or</sup> and hydrophilicity, or a reactive group reactive <sup>with</sup> to an adduct or the like.

In general, such a conventional surface reforming is carried out by making the surface radical using ozone or UV, or ozone in combination with UV, and forming a chemical bond <sup>between</sup> of a main component of a treatment agent <sup>and</sup> with the surface. On the other hand, a desired characteristic is <sup>can be</sup> obtained <sup>attaching</sup> for a moment by sticking a treatment agent, <sup>which itself has a</sup> having the very desired characteristic, itself to the element's surface without making the surface radical, <sup>and</sup> in this case, the continuity is usually lacking. Especially, <sup>with respect to imparting</sup> regarding the hydrophilicity <sup>properties to</sup> for an olefinic resin, <sup>harmless to the</sup> environments, it is only known that, <sup>an</sup> incomplete hydrophilic condition, which is insufficient <sup>for</sup> in the continuity <sup>continuous period</sup> for a long duration, can temporarily be provided by mixing a surfactant with a <sup>hydrophilic</sup> treatment agent ~~for producing hydrophilicity~~ in the presence of a liquid.

On the other hand, an adhesive or a primer is conventionally used to form an additive layer on an element. <sup>In that regard</sup> Regarding them, in order to use a primer such as a silane coupling agent which is bonded to the

surface of an element only by <sup>a</sup>the chemical reaction,  
the element has to be treated to be reactive.

As another type <sup>of a</sup> primer, ~~those which are of similar~~ <sup>can be used</sup> materials to that of an element ~~are available~~ to  
5 utilize the affinity to the element. As such a primer,  
an acid-deformed polypropylene chloride is known, ~~which and~~  
is used at the time when an upper coating layer of a  
polyurethane resin is formed on polypropylene.  
However, in the case where a primer <sup>is made</sup> of a similar  
10 material to that of the surface of an element, the  
element <sup>volume</sup> ~~is consequently~~ increased <sup>S</sup> ~~in the volume and an~~  
~~additionally requires a~~ technique <sup>is required</sup> to form a thin and  
uniform coating. Also, the primer ~~cannot~~ be supplied  
evenly to a fine element or to the inner parts of a  
15 porous body. Especially, the acid-deformed  
polypropylene chloride ~~can not~~ be used in an aqueous  
solution, <sup>because</sup> ~~state~~ as it is insoluble in water, <sup>and</sup> the way of  
using it is limited.

As a result, no material has been available <sup>that</sup> ~~which~~  
20 is soluble in water <sup>so that it can</sup> ~~to be~~ an aqueous solution and can  
be applicable to form a thin and uniform surface  
reforming layer regardless of the shape of the element,  
even among materials different from that of the surface  
of an element.

25 ~~To describe the present invention in relation to~~  
~~the background of the related arts in the relevant~~  
~~field,~~ The present invention is innovative and ~~achieved~~

*is* *stemming from* *action of*  
being based on new findings ~~found by~~ examining the  
conventional technical standards.

*techniques that are* *solids*  
~~The~~ surface reforming *only* based on ~~the~~ chemical  
bonding by radicalizing the surface in a conventional  
manner *can only be used* to treat an extremely narrow plane but *is*  
5 often ~~invalid~~ *cannot be applied* to carry out sufficient and even surface  
reforming of the ~~whole~~ *entire* spherical surface <sup>or</sup> the inner or  
outer surface of a tube. Further, it is especially  
difficult to carry out the surface reforming treatment  
10 for the inside of an element comprising a complicated,  
porous ~~part~~ *portion* such as a sponge, ~~and~~ fibrous composite body,  
and void parts among fibers.

In addition ~~to that~~, in the case where a  
surfactant or the like is added to a liquid, the  
15 surface reforming of an element is not actually carried  
out and the ~~characteristic~~ *specific surface* is lost at the time when the  
surfactant is eliminated and the original  
characteristic of the surface itself ~~is~~ instantaneously  
*re*appears.

20 Moreover, though an olefinic resin has excellent  
~~in~~ water-repelling property *is* *i.e.*, ~~meaning that~~ the contact  
angle <sup>with</sup> to water is 80 degrees <sup>greater</sup> or higher, ~~and~~ *it* is utilized  
in almost all fields, ~~and~~ *is* applicable to a considerably  
wide range of use ~~purposes~~, the surface reforming  
25 method is ~~scarcely available~~ *hardly able* as to provide a desired ~~and~~  
characteristic ~~durable for a long duration~~.

*durable* *surface* The present ~~inventors~~ *invention* have examined ~~as to~~ provide ~~s~~

a method for reforming<sup>2)</sup> surface of any element by  
rationally carrying out surface reforming, at first, of  
an olefinic resin and explicating a method for  
maintaining the reformed characteristic and focused<sup>8</sup>  
5 upon the use of a liquid phase treatment solution  
presupposing that the surface treatment is possible  
even ~~to~~<sup>for</sup> an element with a complicated shape.

~~As new findings of inventors of the present~~  
~~invention,~~ <sup>T</sup>he inventors have found that the balance  
10 between functional groups (e.g. hydrophilic groups) and  
the surface of an element to be treated is well  
controlled to be<sup>m</sup> a desired state by utilizing the  
surface energy in a relation between the surface to be  
treated and a polymer having the functional groups  
15 (e.g. hydrophilic groups), and that the durability of  
the reformed surface and the stability of the quality  
can further be heightened by analyzing the polymer  
itself.

## 20 SUMMARY OF THE INVENTION

The following is the description of the  
technological objects to be solved by the present  
invention. The present invention is neither ~~to~~<sup>||</sup> processing  
an element in the above-described manner ~~or~~<sup>by forming</sup> ~~or~~  
25 radicalizing<sup>S</sup> ~~the characteristic of an element with~~  
ozone or UV rays nor ~~to form a primer coating of such~~<sup>||) my</sup> ~~as~~  
~~a silane coupling agent, which sometimes causes~~  
<sup>using, for example,</sup>

*The present invention*

coating unevenness, ~~but~~ aims mainly to provide an innovative surface reforming method capable of carrying out ~~a~~ desired surface reforming based on a new mechanism and a treatment solution to be used for the method, to provide an element obtained by the method, and to provide the surface structure itself obtained by the surface treatment.

A first purpose of the present invention is to provide a liquid-phase treatment solution capable of carrying out a desired surface treatment ~~to a whole~~ <sup>of entire</sup> inner surface of an element having a complicated shape, such as a porous body and a finely processed element, and a surface reforming method using the treatment solution.

A second purpose of the present invention is to provide a new surface reforming method capable of maintaining the reformed characteristic for a long ~~duration~~ <sup>period of time</sup> as compared with a conventional method for an olefinic resin, <sup>the surface of</sup> ~~which has been supposed to be~~ difficult to ~~be treated for surface reforming~~, and to provide a surface structure itself.

A third purpose of the present invention is to provide a new surface reforming method capable of forming a ~~thin~~ layer <sup>with</sup> of a thickness <sup>on</sup> ~~in~~ a molecular level, preferably a monomolecular level, as a reformed surface itself without changing <sup>the</sup> ~~a~~ structure of an element or with scarcely increasing the weight of the

element and to provide a surface structure itself.

5 A fourth purpose of the present invention is to provide a treatment method with which a desired reforming can freely be carried out by introducing a new mechanism into a surface reforming method ~~itself~~.

A fifth purpose of the present invention is to provide a method for easily manufacturing a surface-reformed element with high productivity.

10 A sixth purpose of the present invention is to provide an innovative method for reforming <sup>an</sup> element's surface utilizing interfacial physical adsorption based on an energy level approximately similar to cleaving of a polymer from the view point of interfacial energy of a group (or groups) of the polymer.

15 A seventh purpose of the present invention is to provide an innovative surface reforming method capable of evenly reforming a circumference of an element, and, at the same time, to provide a surface structure ~~which~~ <sup>that</sup> has not been obtained <sup>in</sup> ~~by~~ <sup>entire</sup> a conventional manner from the view point of the ~~whole~~ circumference of the surface structure itself.

25 Other purposes of the present invention may be understood from the following descriptions, and the present invention can achieve compounded purposes in an optional combination of the above ~~described~~ <sup>aspects</sup> respective purposes.

The following ~~inventions~~ are included in the

present invention in order to achieve the above-described purposes.

One aspect of a surface reforming method of the present invention is a ~~surface reforming~~ method for reforming a part of <sup>a</sup> surface by providing a partial surface, which composes at least a part of the surface of a prescribed element, to be subjected to surface reforming with a functional group. <sup>The method is</sup> ~~for surface reforming~~ and is characterized in that the ~~above-described~~ supply of the functional group to the ~~above-described~~ partial surface is carried <sup>out</sup> by a method involving a first step of supplying, to the ~~above-described~~ partial surface, a liquid containing a polymer, which is different from a constituent material of the partial surface and which composes a first part having <sup>a</sup> the functional group, and a second part having a group with an interfacial energy <sup>that is</sup> of approximately equal to the surface energy of the partial surface but different from the interfacial energy of the forgoing functional group and a second step of orienting the second part of the ~~above-described~~ polymer toward the ~~above-described~~ partial surface and orienting the first part toward the different side from the ~~above-described~~ partial surface.

25 Another aspect of a surface reforming method according to the present invention is a ~~surface reforming~~ method for reforming a part of the surface by



providing a partial surface, which composes at least a part of the surface of a prescribed element, to be subjected to the surface reforming with a functional group ~~for surface reforming~~ <sup>① This method</sup> and is characterized in that ~~the above described~~ supply of the functional group <sup>is</sup> to the ~~above described~~ partial surface ~~is carried by~~ a method involving a first step of supplying, to the ~~above described~~ partial surface, a liquid containing fractionalized (fragmented) products, which are obtained by cleaving of a polymer composing a first part having the above ~~described~~ functional group and a second part having a group with an interfacial energy ~~of that~~ approximately equal to the surface energy of the partial surface but different from the interfacial energy of the forgoing functional group and which contain the ~~above described~~ first part and the ~~above described~~ second part, a second step of orienting the second part of the ~~above described~~ fractionalized products toward the ~~above described~~ partial surface and orienting the first part toward <sup>a</sup> the different side from the ~~above described~~ partial surface, and a third step of at least partially polymerizing the fractionalized products oriented on the ~~above described~~ partial surface by condensation polymerization.

25 One aspect of an element having the surface reformed <sup>in accordance with</sup> by a method of the present invention is an element provided with a polymer compound in a partial

surface composing at least a part of the surface and is characterized in that the ~~above described~~ polymer compound is a material <sup>that</sup> ~~which~~ is either soluble in a solvent or has a main skeleton different from the material at least partially composing the forgoing partial surface and which comprises a first part having a functional group for reforming the ~~above described~~ partial surface and a second part having the interfacial energy different from the interfacial energy of the ~~above described~~ functional group and approximately equal to the surface energy of the ~~above described~~ partial surface <sup>and</sup> ~~the above described~~ second part is oriented toward the ~~above described~~ partial surface and the ~~above described~~ first part is oriented in <sup>a</sup> ~~the~~ direction different from that of the ~~above described~~ partial surface.

Another aspect of an element having the surface reformed <sup>in accordance with</sup> ~~by~~ a method of the present invention is an element provided with a polymer compound in a face made of a polymer material having 80° or <sup>greater</sup> ~~wider~~ contact angle <sup>with</sup> ~~to~~ water. <sup>This element</sup> ~~and~~ is characterized in that the ~~above described~~ polymer compound is a material <sup>that</sup> ~~which~~ is either soluble in a solvent or having <sup>S</sup> a main skeletal structure different from the ~~above described~~ polymer material and which comprises a first part having a hydrophilic group and a second part having the interfacial energy lower than the interfacial energy of

the ~~above described~~ hydrophilic group and approximately equal to the surface energy of the ~~above described~~ face made of the polymer material, and the ~~above described~~ second part is oriented toward the face made of the

5 ~~above described~~ polymer material and the ~~above described~~ first part is oriented in the direction different from that of the face made of the ~~above described~~ polymer material to <sup>impart</sup> ~~give~~ <sup>properties</sup> ~~hydrophilicity~~ <sup>etc</sup> to the face made of the ~~above described~~ polymer material.

10 A fibrous body with <sup>a</sup> ~~reformed~~ surface formed <sup>in accordance</sup> ~~by~~ the <sup>with</sup> present invention is a fibrous body made of a fiber, having an olefinic resin at least in the surface and provided with a polymer compound in the ~~above described~~ surface, <sup>This fibrous body</sup> and is characterized in that the ~~above described~~ <sup>that</sup> polymer compound is a material which is

15 either soluble in a solvent or having <sup>a</sup> ~~a~~ main skeletal structure different from the ~~above described~~ material forming the surface and which is a polyalkylsiloxane comprising a hydrophilic group and the alkyl group of

20 the polyalkylsiloxane is oriented toward the ~~above described~~ surface and the ~~above described~~ hydrophilic group is oriented <sup>in</sup> ~~toward~~ <sup>a</sup> ~~the~~ direction different from the ~~above described~~ surface side to provide the ~~above described~~ surface with hydrophilicity <sup>properties</sup>.

25 One aspect of a method for manufacturing a fiber with <sup>a</sup> ~~reformed~~ surface <sup>in accordance with</sup> ~~by~~ the present invention is a method of manufacturing a fiber having an olefinic

resin at least in the surface and provided with a  
reformed surface having hydrophilicity <sup>properties</sup> in the ~~above~~  
~~described surface and is characterized by comprising~~ <sup>This method comprises</sup>  
a first step of supplying a solution containing a  
5 dissolved alkylsiloxane polymer having a hydrophilic  
group to the ~~above-described~~ surface and a second step  
of orienting the ~~above-described~~ alkylsiloxane to the  
~~above-described~~ surface and orienting the ~~above~~  
~~described~~ hydrophilic group in the <sup>N</sup> different direction  
10 from the ~~above-described~~ surface.

Another aspect of a method of manufacturing a  
fiber with <sup>N</sup> reformed surface <sup>in accordance with</sup> by the present invention is  
a method of manufacturing a fiber having an olefinic  
resin at least in the surface and provided with a  
15 reformed surface having hydrophilicity <sup>properties</sup> in the ~~above~~  
~~described surface and is characterized by comprising~~ <sup>This method</sup> <sup>is</sup>  
a first step of supplying to the ~~above-described~~ surface  
a solution containing dissolved fractionalized products  
obtained by cleaving of an alkylsiloxane polymer having  
20 a hydrophilic group and a second step of condensing the  
~~above-described~~ fractionalized products on the ~~above~~  
~~described~~ surface, orienting the ~~above-described~~  
alkylsiloxane to the ~~above-described~~ surface and  
orienting the ~~above-described~~ hydrophilic group in the  
25 different direction from the ~~above-described~~ surface.

Another aspect of a method of manufacturing a  
fiber with <sup>N</sup> reformed surface <sup>in accordance with</sup> by the present invention is

a method of manufacturing a fiber having an olefinic resin at least in the surface and provided with a reformed surface having hydrophilicity <sup>properties</sup> ~~in the above~~ <sup>This method</sup> ~~described surface and is characterized by comprising~~ <sup>10</sup> a

5 step of forming a fiber surface coated with a treatment solution containing a polyalkylsiloxane having a hydrophilic group, an acid, and an alcohol and a step of drying the treatment solution coating the ~~above~~ ~~described~~ fiber surface at a temperature higher than a

10 room temperature.

Another aspect of a method of manufacturing a fiber with <sup>N</sup> ~~A~~ reformed surface <sup>in accordance with</sup> ~~by~~ the present invention is a method of manufacturing a fiber having an olefinic resin at least in the surface and provided with a

15 reformed surface having hydrophilicity <sup>properties</sup> ~~in the above~~ ~~described surface~~ and is characterized by comprising a step of forming a fiber surface coated with a treatment solution containing a polyalkylsiloxane having a hydrophilic group, an acid, an alcohol, and water and a

20 step of drying the treatment solution coating the ~~above~~ ~~described~~ fiber surface while making the ~~above~~ ~~described~~ surface hydrophilic by orienting the ~~above~~ ~~described~~ hydrophilic group in the ~~opposed~~ <sup>N</sup> direction <sup>opposite</sup> to the ~~above~~ ~~described~~ surface.

25 Another aspect of a surface reforming method according to the present invention is a surface reforming method of the surface of a prescribed element, <sup>which method</sup>

*Comprises*  
and is characterized by ~~comprising~~ a first step of  
supplying, to the ~~above-described~~ surface, a liquid  
containing a diluted sulfuric acid, a volatile agent  
for reforming the affinity with the element's surface and  
5 a treatment agent of a polymer comprising a second part  
having a group with an interfacial energy approximately  
equal to the surface energy of the ~~above-described~~  
surface and a first part having a group with an  
interfacial energy different from the ~~above-described~~  
10 interfacial energy, a second step of removing the ~~above-~~  
~~described~~ agent for reforming the affinity by heating  
the resultant surface, a third step of cleaving the  
polymer in the ~~above-described~~ treatment agent by  
concentrating the ~~above-described~~ diluted sulfuric acid  
15 to a concentrated sulfuric acid, and a fourth step of  
condensing the ring-opened polymer on the ~~above-~~  
~~described~~ surface and at the same time orienting the  
second part of the polymer toward the ~~above-described~~  
surface and orienting the first part ~~in the different~~  
20 *different* side from the ~~above-described~~ surface.

Another aspect of a surface reforming method  
according to the present invention is a method for  
reforming the surface of an element by introducing a  
functional group to the forgoing surface, *which method*  
25 characterized by involving a step of condensing  
fractionalized products comprising a second part having  
a group with an interfacial energy approximately equal

to the surface energy of the ~~above described~~ surface  
and a first part having the ~~above described~~ functional  
group and obtained <sup>in</sup> by cleaving a polymer compound  
having the ~~above described~~ first part and the ~~above~~  
5 ~~described~~ second part <sup>so that</sup> ~~in the condition wherein~~ the  
fractionalized products are oriented based on the  
affinity of the group having the interfacial energy  
approximately equal to the surface energy with the  
~~above described~~ surface.

10 Another aspect of an element having a <sup>surface</sup> reformed  
~~surface~~ by the present invention is an element having a  
reformed surface into which a functional group is  
introduced, <sup>This element has</sup> ~~and is characterized by bearing~~ a condensate  
substance of fractionalized products in the ~~above~~  
15 ~~described~~ surface <sup>2</sup> and ~~the above described~~  
fractionalized products comprise a second part having a  
group with an interfacial energy approximately equal to  
the surface energy of the ~~above described~~ surface and a  
first part having the ~~above described~~ functional group ~~and~~  
20 ~~are~~ obtained by cleaving a polymer compound having the  
~~above described~~ first part and the ~~above described~~  
~~second part~~ <sup>The fractionalized products so that</sup> ~~and are condensed in the condition wherein~~  
~~the fractionalized products~~ <sup>are</sup> are oriented based on the  
affinity of the group having the interfacial energy  
25 approximately equal to the surface energy with the  
~~above described~~ surface.

Another aspect of an element having a <sup>surface</sup> reformed

~~surface~~ by the present invention is an element having a circumferential part of a curved face forming a closed circular shape as an outer circumferential cross-section <sup>This element</sup> and is characterized in that the ~~above~~ <sup>portion</sup> described outer circumferential part has a ~~part~~ coated with a film containing a polymer and circularly surrounded with the film in one closed turn as to reform the forgoing surface part <sup>1</sup> and <sup>2</sup> the ~~above~~ <sup>first</sup> described polymer compound is a material which is soluble in a solvent or has a main skeletal structure different from the material of the surface of the element and which comprises a first part having a functional group for reforming the ~~above-described~~ surface and a second part having the interfacial energy different from that of the ~~above-described~~ functional group and approximately equal to the surface energy of the ~~above-described~~ surface <sup>1</sup> and the ~~above-described~~ second part is oriented toward the ~~above-described~~ surface and the ~~above-described~~ first part is oriented in <sup>a</sup> the direction different from that of the ~~above-described~~ surface.

Another aspect of a surface reforming method of the present invention is a ~~surface-reforming~~ method for reforming the hydrophobic surface of an element to ~~be~~ <sup>make it</sup> hydrophilic, <sup>This method comprises</sup> and is characterized by ~~involving~~ <sup>attaching</sup> a step of sticking, to the ~~above-described~~ hydrophobic surface, fractionalized products comprising a hydrophilic group



*The fractionalized products are*

and a hydrophobic group and obtained by cleaving a polymer compound having the ~~above described~~ hydrophilic group and the ~~above described~~ hydrophobic group in a manner that ~~The above described~~ hydrophobic group is oriented in the surface side of the ~~above described~~ hydrophobic surface and the ~~above described~~ hydrophilic group is oriented in <sup>the</sup> direction different from that of the hydrophobic group.

Another aspect of an element having a <sup>surface</sup> reformed <sup>in accordance with</sup> surface by the present invention is an element having a hydrophobic surface <sup>that is</sup> which is reformed to be a hydrophilic surface, and to which ~~F~~ fractionalized products comprising a hydrophilic group and a hydrophobic group, <sup>which are</sup> and obtained by cleaving a polymer compound having the ~~above described~~ hydrophilic group and the ~~above described~~ hydrophobic group, are <sup>attached</sup> stuck in <sup>so</sup> a manner that the ~~above described~~ hydrophobic group is oriented in the surface side of the ~~above described~~ hydrophobic surface and the ~~above described~~ hydrophilic group is oriented in <sup>the</sup> direction different from that of the hydrophobic group.

A surface treatment solution to be used for the surface reforming according to the present invention is a ~~surface treatment solution to be used for a surface reforming method for carrying out surface reforming by~~ <sup>that</sup> supplying a functional group <sup>for</sup> ~~for reforming to a partial surface to be reformed composing at least a part of the~~

*This solution*

~~surface of a proscribed element~~ and is characterized by containing a polymer provided with a first part having a functional group and a second part having the interfacial energy different from that of the ~~above~~  
5 ~~described~~ functional group and approximately equal to the surface energy of the ~~above described~~ partial surface, a volatile solvent having sufficient wettability to the ~~above described~~ element and being a good solvent <sup>for</sup> to the polymer, and <sup>being able to serve as</sup> a cleaving catalyst <sup>for</sup> of ~~the above described~~ polymer.  
10

The surface treatment solution may further contain a volatile solvent <sup>that is not wettable</sup> having ~~no wettability~~ to the ~~above~~  
~~described~~ element and <sup>in</sup> being a good solvent <sup>for</sup> to the ~~above~~  
~~described~~ polymer. A method of producing such a  
15 surface treatment solution is characterized by dissolving the ~~above described~~ polymer in a volatile solvent having sufficient wettability to the ~~above~~  
~~described~~ element and being a good solvent <sup>for</sup> to the ~~above~~  
~~described~~ polymer and then <sup>ad</sup> mixing a volatile solvent  
20 having no wettability to the ~~above described~~ element and being a good solvent <sup>for</sup> to the ~~above described~~ polymer to the resultant solution.

Another aspect of a surface reforming method according to the present invention is a ~~surface~~  
25 ~~reforming~~ method for carrying out surface reforming for a partial surface of an element <sup>which method</sup> and is characterized by reforming the surface by carrying out, on the ~~above~~

~~described~~ partial surface, condensation polymerization of ring-opened polymers oriented based on the affinity of the interfacial energy of a group similar to the surface energy of the partial surface of the element.

5 Another aspect of a surface reforming method according to the present invention is a ~~surface reforming~~ method for ~~carrying out surface reforming for~~ a partial surface of an element using a liquid-phase polymer, <sup>This method</sup> and is characterized by involving a  
10 condensation step ~~to be~~ carried out on the ~~above~~ ~~described~~ partial surface by condensation-polymerizing fractionalized products of a polymer, <sup>which</sup> comprises a first group having a functional group <sup>that can undergo a</sup> ~~possible to be~~ ring-opened <sup>we can be</sup> and <sup>can be</sup> condensation polymerizable, and a second  
15 group having an interfacial energy <sup>which</sup> approximately equal to the surface energy of the partial surface of the element.

Another aspect of an element of the present invention is an element <sup>that</sup> ~~which~~ has a surface comprising  
20 at least an olefinic resin, <sup>The surface is</sup> ~~and~~ reformed by being made hydrophilic and is characterized by having a liquid-contacting surface structure having, practically <sup>in</sup> ~~in~~  
<sup>a</sup> reciprocally <sup>fashion,</sup> a hydrophilic group with a relatively long chain and a hydrophobic group with a relatively short  
25 chain ~~on the above described element surface~~ <sup>This reformed surface</sup> ~~and formed~~ <sup>coats the surface</sup> ~~by forming an element surface coated with a treatment~~ <sup>a</sup> solution containing a polymer having ~~the~~ hydrophilic

group and a group with an interfacial energy approximately equal to the surface energy of the element surface comprising at least the ~~above-described~~ olefinic resin as a constituent component, a diluted sulfuric acid as a cleaving catalyst <sup>for</sup> of the ~~above-described~~ polymer, and an alcohol, evaporating the treatment solution coating the ~~above-described~~ element surface and simultaneously concentrating the diluted sulfuric acid to be a concentrated sulfuric acid on the ~~above-described~~ element surface to ring-open the ~~above-described~~ polymer, and then condensation-polymerizing the ring-opened products.

#### BRIEF DESCRIPTION OF THE DRAWINGS

15 FIGS. 1A and 1B are schematic ~~figures~~ <sup>ONS</sup> illustrating the adhesion state of a polymer as a surface reforming agent formed on the ~~object surface to be reformed~~ of an element (a substrate) <sup>to be reformed by</sup> ~~to the element surface~~ in a surface treatment method of the present invention, and

20 FIG. 1A ~~is a figure~~ <sup>is</sup> illustrating the case where a polymer has a first group as a functional group and a second group for adhering to the element surface both in the side chains, ~~and~~ FIG. 1B ~~is a figure~~ <sup>is</sup> illustrating the case where the second group is contained in the

25 main chain;

FIG. 2 is a schematic ~~figure~~ <sup>on</sup> illustrating the state of applying a treatment solution containing a

polymer as a surface reforming agent and forming a coating layer on the substrate in a surface reforming method of the present invention;

FIG. 3 is a generalized ~~figure~~ illustrating <sup>on of</sup> the step of partially removing a solvent in the coating layer formed on a substrate and containing a polymer as a surface reforming agent in a surface reforming method of the present invention;

FIGS. 4A and 4B are generalized ~~figures~~ illustrating <sup>on of</sup> the step of <sup>a</sup> partial dissociation of a polymer as a surface reforming agent caused by an acid added to a treatment solution following the step of partially removing a solvent in the coating layer containing the polymer as ~~a surface reforming agent~~;

FIG. 5 is a generalized ~~figure~~ illustrating <sup>on of</sup> the step of orienting a polymer as a surface reforming agent or its dissociated and fractionalized products following the step of further removing a solvent in the coating layer containing the polymer as ~~a surface reforming agent~~;

FIG. 6 is a generalized ~~figure~~ illustrating <sup>on of</sup> the step of orienting a polymer as a surface reforming agent or its dissociated and fractionalized products and <sup>attaching</sup> ~~sticking~~ and fixing them on the surface following the step of drying and removing a solvent in the coating layer;

FIG. 7 is a generalized ~~figure~~ illustrating <sup>on of</sup> the

step of re-bonding dissociated and fractionalized products <sup>with</sup> one another derived from a polymer as a surface reforming agent, which is <sup>attached</sup> stuck and fixed to and on the surface, by <sup>a</sup> condensation reaction;

5           FIG. 8 is a generalized ~~figure~~ <sup>on</sup> illustrating <sup>an</sup> an embodiment of a surface reforming method of the present invention applied to a hydrophobic surface to <sup>change</sup> convert ~~the surface to be~~ hydrophilic <sup>a</sup> and <sup>surface, which illustration shows</sup> showing the effect of adding water to a treatment solution;

10           FIGS. 9A and 9B are schematic ~~figures~~ <sup>on</sup> illustrating <sup>of</sup> an embodiment of a surface reforming method of the present invention applied to ~~the treatment of making~~ <sup>make</sup> a hydrophobic PP container inner wall face ~~be~~ hydrophilic <sup>on</sup> and FIG. 9A is a schematic ~~figure~~ <sup>on</sup> illustrating <sup>of</sup> the untreated inner wall face of the PP container, and FIG. 9B is a schematic ~~figure~~ <sup>on</sup> illustrating <sup>of</sup> the inner wall face coated with a hydrophilic agent following the <sup>hydrophilic</sup> treatment ~~of providing hydrophilicity~~;

20           FIGS. 10A, 10B, 10C and 10D are ~~figures~~ <sup>on</sup> illustrating <sup>of</sup> a PE/PP fibrous body usable for an ink absorbent in an ink tank, and FIG. 10A is a schematic ~~figure~~ <sup>on</sup> illustrating <sup>of</sup> the utilization embodiment as an ink absorbent in an ink tank, and FIG. 10B, FIG. 10C, and FIG. 10D are schematic ~~figures respectively~~ <sup>respectively,</sup> illustrating <sup>on</sup> the <sup>entire</sup> whole shape of the PE/PP fibrous body and the orientation direction F1 of the fibers and the direction F2 <sup>perpendicular</sup> ~~rectangular~~ to the direction F1, the ~~above~~

25

~~described~~ PE/PP fibrous body in the state before formation by thermal fusion, and the ~~above described~~ PE/PP fibrous body in the state after formation by thermal fusion;

5           FIGS. 11A and 11B are ~~figures illustrating~~ one example of a cross~~section structure~~ of a PE/PP fibrous body shown in the FIGS. 10A to 10D, ~~and~~ FIG. 11A is an example of approximately concentric~~ally~~ coating<sup>of</sup> a PP core material with a PE sheath material, ~~and~~ FIG. 11B is  
10   a schematic ~~figure~~ illustrating<sup>on of</sup> the example of eccentric~~ally~~ coating<sup>ed</sup> a PP core material with a PE sheath material;

          FIGS. 12A, 12B, 12C, 12D, 12E and 12F are ~~figures~~ illustrating<sup>e</sup> an ~~embedment of~~ application<sup>of</sup> a surface  
15   reforming method of the present invention to ~~the~~ ~~treatment for making~~<sup>e n</sup> hydrophobic surface of the PE/PP fibrous body shown in FIGS. 10A to 10D ~~be~~ hydrophilic<sup>o</sup> ~~and~~ FIG. 12A is a schematic ~~figure~~ of an untreated fibrous body<sup>o</sup> FIG. 12B schematically illustrates the  
20   step of immersing the fibrous body in a treatment solution for making the surface ~~be~~ hydrophilic<sup>o</sup> ~~and~~ FIG. 12C schematically illustrates the step of pressurizing the fibrous body after immersion and removing<sup>u n</sup> the excess treatment solution. FIGS. 12D to  
25   12F are partially magnified figures of FIGS. 12A to 12C, respectively;

          FIGS. 13A, 13B, 13C, 13D, 13E and 13F are ~~figures~~

illustrating<sup>e</sup> the steps successive to the steps  
illustrated in FIGS. 12A to 12C and FIG. 13A is a  
schematic ~~figure~~ illustrating<sup>On</sup> the coating layer formed  
on the surface of a fibrous body. FIG. 13B  
5 schematically illustrates the step of drying and  
removing a solvent contained in the coating layer and  
FIG. 13C is a schematic ~~figure~~ illustrating the coating  
on the surface of the fibrous body with an agent for  
making the surface hydrophilic; FIGS. 13D to 13F are  
10 partially magnified ~~figures~~ of FIGS. 13A to 13C,  
respectively;

FIG. 14 is a SEM photograph of <sup>(magnification)</sup> 150 ~~magnifications~~  
~~substituting the figure~~ illustrating untreated PP-PE  
fibrous shapes and their surface state of a reference  
15 example (an untreated PP-PE fibrous absorbent);

FIG. 15 is a SEM photograph of <sup>(magnification)</sup> 500 ~~magnifications~~  
~~substituting the figure~~ illustrating untreated PP-PE  
fibrous shapes and their surface state of a reference  
example (an untreated PP-PE fibrous absorbent);

20 FIG. 16 is a SEM photograph of <sup>(magnification)</sup> 2,000 ~~magnifications~~  
~~magnifications substituting the figure~~ illustrating  
untreated PP-PE fibrous shapes and their surface state  
of a reference example (an untreated PP-PE fibrous  
absorbent);

25 FIG. 17 is a SEM photograph of <sup>(magnification)</sup> 150 ~~magnifications~~  
~~substituting the figure~~ illustrating acid-treated PP-PE  
fibrous shapes and their surface state of a comparison



example 4 (PP-PE fibrous absorbent treated only with an acid and an alcohol);

FIG. 18 is a SEM photograph of <sup>(magnification</sup> ~~150)~~ ~~magnifications~~ ~~substituting the figure~~ illustrating treated PP-PE fibrous shapes and their surface state of ~~an~~ example 2 (a PP-PE fibrous absorbent treated to be hydrophilic);

FIG. 19 is a SEM photograph of ~~500~~ <sup>(magnifications 370)</sup> ~~substituting the figure~~ illustrating treated PP-PE fibrous shapes and their surface state of ~~an~~ example 2 (a PP-PE fibrous absorbent treated to be hydrophilic);

FIG. 20 is a SEM photograph of ~~2,000~~ <sup>(magnifications 3000)</sup> ~~substituting the figure~~ illustrating treated PP-PE fibrous shapes and their surface state of an example 2 (a PP-PE fibrous absorbent treated to be hydrophilic);

FIGS. 21A, 21B, 21C and 21D are ~~figures~~ <sup>e</sup> illustrating an example of application of the surface reforming method of the present invention to the ~~treatment of~~ making the surface of a PP fine particle ~~be~~ hydrophilic <sup>and</sup> and FIG. 21A is a schematic ~~figure~~ of an untreated PP fine particle; FIGS. 21B and 21C are respectively schematic ~~figures~~ illustrating the PP fine particle coated with an agent for making the surface hydrophilic ~~by the treatment of making the surface~~ hydrophilic <sup>(f)</sup> and FIG. 21D is a schematic ~~figure~~ illustrating the coating containing the agent for making the surface hydrophilic and formed on the

surface, which is a curved plane of the fine particle;

FIG. 22 is a schematic ~~figure~~ illustrating the step of stirring and drying a PP fine particle coated with a treatment solution by warm air blow;

5        FIG. 23 is a ~~step-figure~~ <sup>flow chart</sup> illustrating one example of a manufacturing step of an element having a ~~reformed surface~~ <sup>surface</sup> by the present invention; and

FIG. 24 is a ~~figure~~ <sup>on of</sup> schematically illustrating one example of a presupposed distribution of a hydrophilic group and a hydrophobic group in the surface subjected to the surface reforming treatment by the present invention.

10

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

15        The surface modification method of the present invention allows <sup>to attain</sup> the desired surface modification of an element by attaching a polymer (or <sup>a</sup> finely fractionalized (fragmented) product thereof) to the surface <sup>of</sup> the element ~~has~~ in a specific orientation, while

20        utilizing the functional group or the like, ~~which the molecule contained in~~ the material constituting the element ~~surface has~~, to impart the properties associated with the polymer (or <sup>a</sup> finely fractionalized product thereof) to the surface.

25        The "element" <sup>as</sup> used herein, means <sup>a structure</sup> ~~the one~~ made of various materials and <sup>having</sup> taking a specific external shape. Therefore <sup>2</sup> It has an exposed external surface

associated with the external shape. Moreover, it may contain voids, cavities or hollows, each containing the section, which is in communication with the outside. The internal surface (internal wall surface), which divides the section, may be the partial surface to be treated by the surface modification method of the present invention. The hollow may have an internal surface by which it is fractionalized, and may be completely isolated from the outside. However, such a hollow can be subjected to the treatment by the present invention, so long as the surface treatment solution can be applied to its inside before the modification treatment and <sup>the hollow</sup> becomes isolated from the outside after the treatment.

15        The surface modification method of the present invention is applicable to any surface <sup>an</sup> ~~out~~ of ~~all~~ <sup>2</sup> surfaces a varying element has <sup>2</sup> with which the surface treatment solution can be brought into contact with from the outside without damaging the element shape. <sup>of the</sup>

20        The partial surface to be treated includes <sup>an</sup> external surface of the element, internal surface in communication therewith, and both <sup>of these surfaces</sup>. Modification of properties of partial surface(s) selected and fractionalized from the surface to be treated is within

25        the scope of the present invention. Depending on the selection, the embodiment ~~of~~ selecting the external surface of an element and its internal surface in

communication therewith is included in the modification of the desired partial surface region.

In the method of the present invention, a partial surface, i.e., at least a part of <sup>the</sup> surface, <sup>of</sup> an element ~~has~~, to be modified is treated. In other words, the surface of an element selected as required is treated <sup>in its entirety or</sup> ~~partly or totally~~.

The element shape is not limited. <sup>The element</sup> ~~It~~ may be sheet-shaped, yarn-shaped, fibrous, spherical, particulate, tubular or in <sup>any</sup> other shapes, including a distorted one. The purpose of the element is also not limited. The surface modification method of the present invention is applied to an element in accordance with its specific purpose. The element is generally made of a material suitable for its <sup>intended</sup> purpose, e.g., plastic, resin, metal, glass, paper or leather, which utilizes the natural material, or a material similar thereto, e.g., synthetic leather. The surface modification method of the present invention is applicable, in principle, to any surface of <sup>any</sup> elements made of various materials.

The "surface <sup>of</sup> an element ~~has~~" used herein includes the surface the element <sup>has</sup> ~~itself~~ originally ~~has~~ and the element surface treated by a certain method.

The "finely fractionalized polymer" used herein includes <sup>a polymer</sup> ~~from the polymer~~ <sup>one</sup> fractionalized at its part to the monomer for the polymer. Viewed from the preferred

embodiments, it includes any type of polymer cleaved in the presence of a cleaving catalyst, e.g., acid. The "polymer made into film" includes a substantial film and film oriented differently region by region relative to the two-dimensional plane.

The principle of surface modification is described more concretely by <sup>showing a</sup> ~~taking~~ modification of a surface comprising <sup>a</sup> single material as ~~the example~~ to facilitate <sup>the</sup> explanation of the principle.

It is preferable that the "polymer" used herein comprises two sections, the first <sup>section</sup> ~~one~~ having a functional group and <sup>the</sup> second <sup>section</sup> ~~one~~ having <sup>an</sup> interfacial energy, which is different from that of the functional group of the first section and almost equivalent to <sup>the</sup> surface energy of the element to which it is to be attached, and that it is different from the material, which constitutes the element's surface. The desirable polymer may be adequately selected from those having <sup>an</sup> interfacial energy almost equivalent to <sup>the</sup> surface energy of the element to which it is to be attached, depending on the components of the element. It is more preferable that the "polymer" for this invention can be cleaved and subsequently condensed. It may have a functional group in addition to the two sections described above. In such a case, it is preferable, when <sup>a</sup> ~~hydrophilicization~~ treatment is <sup>applied</sup> ~~taken~~ as an ~~example~~, that the hydrophilic group as the functional

<sup>used</sup>

group <sup>has a</sup> ~~is of~~ longer chain than any <sup>other</sup> functional group ~~other than that~~ in the above first or second section, which is more hydrophobic than the above hydrophilic group.

- 5 The portion to be surface-treated by the present invention may be composed of a single material or a composite material of two or more types of materials, ~~and also may be~~ <sup>compound</sup> of a polymer different from the constituent of the element ~~in consideration of material for the surface to be treated.~~
- 10

#### (Principle of Surface Modification)

- Surface modification of an element by the present invention is effected by utilizing a polymer serving as the surface modifier, which comprises the main skeleton (generic term for one or more groups in the main or side chain) to which a group is bound. The main skeleton having <sup>S. an</sup> interfacial energy <sup>that is</sup> almost equivalent to the surface (interfacial) energy of the element surface (substrate surface) and the group having <sup>S. an</sup> interfacial energy different from <sup>the</sup> surface (interfacial) energy of the element surface, wherein the main skeleton helps the polymer <sup>to</sup> attach to the element surface, while the group helps <sup>to</sup> form the polymer film (coating layer) orienting <sup>ed</sup> outward from the element surface.
- 15
- 20

- 25 The polymer serving as the surface modifier for the present invention, when viewed from a different angle, has two types of groups. The first <sup>group has</sup> one having

On affinity essentially different from that of the group exposed to the element surface before modification<sup>2</sup> and  
The second <sup>group has an</sup> ~~one having~~ affinity essentially similar to that of the exposed group and <sup>is</sup> ~~being~~ contained in the repeating unit in the main skeleton.

FIGS. 1A and 1B schematically illustrate the representative orientation types<sup>2</sup> FIG. 1A <sup>shows</sup> modeling a polymer with <sup>a</sup> the first group 1-1 and <sup>a</sup> second group 1-2 bonded as the side chains to the main chain 1-3 of the surface modifier, while FIG. 1B <sup>shows</sup> a polymer with the second group 1-2 constituting the main chain 1-3 itself and the first group 1-1 constituting the side chain.

In the orientation shown in FIGS. 1A and 1B, the outermost (outside) surface of the substrate 6, which constitutes the surface of the element to be surface-modified, has the first group 1-1 <sup>with an</sup> ~~having~~ interfacial energy different from surface (interfacial) energy of the substrate 6<sup>2</sup> oriented on the surface. As a result, the properties associated with the first group 1-1<sup>2</sup> ~~having interfacial energy different from surface~~  
~~(interfacial) energy of the substrate 6~~ are utilized to modify the element surface. It should be noted that <sup>that</sup> ~~the~~ surface (interfacial) energy of the substrate 6 is determined by the material/molecule ~~which~~ constitutes the surface and group 5 exposed to the surface. More concretely, in the example shown in FIGS. 1A and 1B, the first group 1-1 works as the functional group for

surface modification to make the <sup>surface of the</sup> substrate 6 ~~surface~~  
hydrophilic, when the substrate ~~6~~ surface is  
hydrophobic and first group 1-1 is hydrophilic. When  
the first group 1-1 is hydrophilic and group 5 exposed  
5 to the surface on the side of substrate 6 is  
hydrophobic, e.g., when <sup>or</sup> polysiloxane is used as  
described <sup>below</sup> ~~later~~, it is considered that the conditions  
shown in FIG. 24 are present on the substrate ~~6~~  
surface. Under these conditions, it is possible to  
10 adjust, when water or <sup>an</sup> aqueous solution mainly  
comprising water is passed over the modified <sup>surface of the</sup> substrate  
6 ~~surface~~, the flow conditions or <sup>the</sup> rate at which <sup>the</sup> water  
or <sup>the</sup> aqueous solution is passed by adjusting the balance  
between the hydrophilic and hydrophobic groups on the  
15 surface of substrate 6 ~~modified~~. Such a surface  
structure allows to alternately arrange the functional  
group supplied from the polymer P and the other group  
having properties different from those of the  
functional group on the substrate surface (element  
20 surface to be treated), to produce the above effect  
when the functional group is hydrophilic and the other  
group is hydrophobic.

These surface conditions may be produced suitably  
by the methods used <sup>in</sup> ~~for~~ Examples ~~later~~ described, <sup>below</sup>  
25 although not limited thereto. These conditions may be  
suitably applied to a variety of materials and  
elements, e.g., tubes and vessels for handling liquid,  
to produce the above effect by adjusting the balance



between the hydrophilic and hydrophobic groups. In such a case, the functional group can have a longer chain than the other group.


In particular, when the element surface structure is fibrous or the like, as shown in FIG. 24, the hydrophilic group 1-1 is a polymer group and is longer than the methyl group (hydrophobic group) in the side chain on the same side. Therefore, when an aqueous solution is passed over the element, the hydrophilic group 1-1 slants toward the element surface (or inner plane) under the influence of the flow rate (and, at the same time, substantially covers the methyl group). As a result, resistance to flow is greatly decreased. Conversely, when the aqueous solution is to be held over the element surface, the hydrophilic group 1-1 stands against the solution, i.e., oriented in the direction perpendicular to the element surface (or inner plane), as a result of which the methyl group is exposed to the fiber surfaces, making hydrophilicity characteristics predominant over the hydrophobicity at the intra-molecular level. Therefore, a sufficient quantity of the solution can be held. The polymer preferably has many (at least two or more) hydrophilic groups to secure the function of the hydrophilic group 1-1. This is illustrated by an example, which uses polyoxyalkylene-poly(dimethyl siloxane) having the hydrophilic group 1-1 with a number of -C-O-C- bonds and -OH group as the

terminal group. When the polymer has <sup>a</sup>the methyl group replaced by another hydrophobic group, the hydrophilic group preferably has a higher molecular weight than the hydrophobic group, to occupy a larger space. In other words, it is preferable that a balance is produced in such a way that hydrophilicity <sup>properties are</sup> is predominant over hydrophobicity. <sup>properties</sup>

The surface structure coming into contact with water in the present invention is applicable, as required, to the balanced hydrophilic and hydrophobic groups handling liquid other than water. For example, the element may be coated with a polymer P having the <sup>a</sup> longer-chain hydrophilic group and <sup>a</sup> shorter-chain hydrophobic group arranged alternately for the surface coming into contact with a liquid to be held over the surface.

When the substrate 6 is <sup>made</sup> of polypropylene and polymer P is polyoxyalkylene-poly(dimethyl siloxane), the group 5 exposed to the <sup>surface of the</sup> substrate 6 surface is a methyl ( $-\text{CH}_3$ ) group, and the substrate 6 has <sup>a</sup> surface energy of approximately 23 dyn/cm, due to the methyl group, which has <sup>a</sup> surface energy of approximately 23 dyn/cm. The poly(dimethyl siloxane) section of the polymer P of polyoxyalkylene-poly(dimethyl siloxane), having <sup>a</sup> methyl ( $-\text{CH}_3$ ) group facing the outside, has <sup>a</sup> surface energy of approximately 23 dyn/cm. It is almost equivalent to that of the substrate 6, due to

methyl group.

The polyoxyalkylene of polyoxyalkylene-  
poly(dimethyl siloxane) has <sup>an</sup> higher surface energy than  
the substrate 6, due to <sup>low</sup> -OH group as the terminal group  
5 (surface energy: 42 to 44 dyn/cm) and <sup>an</sup> oxyalkylene chain  
(-CH<sub>2</sub>-O-CH<sub>2</sub>-). 

Therefore, when the substrate 6 is of  
polypropylene and polymer P is polyoxyalkylene-  
poly(dimethyl siloxane) (shown in FIGS. 1A and 1B), the  
10 poly(dimethyl siloxane) section serves as the main  
chain 1-3, methyl group in the poly(dimethyl siloxane)  
section as the second group 1-2, and polyoxyalkylene  
section as the first group 1-1 (side chain).

One of the methods for producing the element  
15 having the modified surface shown in FIGS. 1A and 1B is  
<sup>specifically</sup> concretely described. It uses an improver, which is a  
good solvent for the polymer as the surface modifier,  
and improves wettability of the treatment agent with  
the substrate. This method spreads the treatment  
20 solution (surface modifier solution) 8, in which the  
polymer ~~as the surface modifier~~ is uniformly dissolved,  
over the substrate surface, and orients the polymer ~~as~~  
~~the surface modifier~~ as described above, while removing  
the solvent <sup>from</sup> in the treatment solution 8.

25 More <sup>specifically</sup> concretely, a surface treatment solution is  
prepared by dissolving a given quantity of the polymer  
and cleavage catalyst in a solvent, which is a good

solvent for the polymer and sufficiently wettable with the substrate surface. It preferably contains pure water, when the functional group serves as the hydrophilic group. The substrate is coated with the above solution on the surface, and <sup>is</sup> treated by evaporation/drying (e.g., in an oven at 60°C) to remove the solvent in the surface treatment solution.

It is preferable for the present invention to use an organic solvent <sup>that</sup> which is sufficiently wettable with <sup>on</sup> the substrate 6 surface and <sup>it</sup> dissolves the polymer P as the surface modifier, in order to facilitate uniform coating of the surface with the polymer for the surface modification. One of its <sup>the</sup> other effects <sup>of the organic solvent</sup> is to keep the polymer P uniformly dispersed in the liquid layer spread over the surface and sufficiently dissolved therein, even <sup>when</sup> it is concentrated as <sup>via</sup> the solvent is evaporated. <sup>ion</sup> In addition, the polymer P as the surface modifier is uniformly spread over the <sup>surface of the</sup> substrate 6 surface, because of sufficient wettability <sup>to</sup> of the surface treatment solution <sup>As a</sup> with the <sup>to</sup> result, <sup>if the surface</sup> that the surface is uniformly coated with the polymer, even it has a complex shape.

The surface treatment solution 8 may be prepared by two types of solvents. <sup>Type is</sup> The first one <sup>being</sup> wettable <sup>to</sup> with the <sup>of the</sup> substrate 6 surface, volatile and a good solvent for the polymer P, and <sup>type</sup> The second one, although <sup>being</sup> a good solvent, <sup>is</sup> less wettable <sup>to</sup> with the substrate <sup>surface of the</sup>

6 ~~surface~~ and less volatile than the first <sup>type</sup> one. One of the examples is a combination of isopropyl alcohol and water, described <sup>below</sup> later, for the polyolefin-based resin serving as the surface <sup>of</sup> the substrate, which is  
5 coated with polyoxyalkylene-poly(dimethyl siloxane) as the polymer.

Addition of an acid 7 as the cleavage catalyst to the surface treatment solution is considered to bring about the following effects. For example, during the  
10 evaporation/drying step of the surface treatment solution, the acid component increases in concentration as the solution components evaporate. The acid ~~of whose~~ increased concentration under heating accelerates <sup>the</sup> partial decomposition (cleavage) of the polymer P as  
15 the surface modifier and production of the finely fractionalized polymer P, allowing them to be oriented in the finer portions on the <sup>surface of the</sup> substrate 6 ~~surface~~. Another effect is expected. Recombination of the cleaved sections of the polymer P during the final  
20 stage of the evaporation/drying step accelerates <sup>the</sup> formation of the film (coating) of the polymer produced as a result of the recombination, preferably ~~the a~~ monomolecular film.

Still another effects <sup>It is obtaining a</sup> is expected, <sup>cleaned surface</sup> ~~the~~  
25 substrate 6 ~~surface~~. The acid component of increased concentration, as a result of evaporation of the solvent during the evaporation/drying of the surface

treatment solution 8, more efficiently removes impurities from the substrate <sup>8</sup> surface and the vicinity thereof, <sup>thereby cleaning</sup> ~~to clean the substrate 6~~ surface.

The cleaned surface is expected to promote physical  
5 adhesion between the substrate material/molecules and polymer as the surface modifier.

The acid <sup>whose</sup> ~~of~~ increased concentration under heating partly decomposes the substrate surface, producing ~~the~~ active sites thereon, which may cause ~~the~~ auxiliary  
10 reactions between these sites and <sup>the</sup> ~~finely~~ fractionalized (cleaved) polymer, described above. Depending on conditions, chemical adsorption of the auxiliary surface modifier on the substrate partly helps stabilize adhesion of the surface modifier to the  
15 substrate.

The main skeleton of the surface modifier (including the hydrophilicization treatment solution 8), having <sup>the</sup> ~~the~~ surface energy almost equivalent to that of the substrate 6, is cleaved, and the resultant finely  
20 fractionalized parts are condensed with each other to form a polymer film on the <sup>surface of the</sup> ~~substrate 6~~ ~~surface~~. Formation of the polymer film is explained by referring to FIGS. 2 to 8 for the case where the functional group 1-1 is hydrophilic to impart hydrophilicity <sup>characteristics</sup> ~~ity~~ to the  
25 hydrophobic substrate surface. The hydrophilic group <sup>is a group</sup> ~~means the one~~ having a structure <sup>that</sup> ~~which~~ can impart hydrophilicity <sup>characteristics</sup> as the whole group. It includes a

hydrophilic group itself, and even a group having a hydrophobic chain or hydrophobic group, so long as it is substituted with a hydrophilic group or the like to be serviceable as a group capable of imparting

5 hydrophilicity. *Characteristics*

FIG. 2 is an enlarged view illustrating the hydrophilicization treatment solution 8 spread over the substrate surface. At this stage, ~~the~~ polymers P1 to P4 as the hydrophilicization agent ~~in the~~ hydrophilicization treatment solution 8 and acid 7 are uniformly dissolved in the hydrophilicization treatment solution 8 over the <sup>surface of the</sup> substrate 6 ~~surface~~. FIG. 3 is an enlarged view illustrating the drying step for the hydrophilicization treatment solution spread over the substrate surface. During the drying step under heating, the acid <sup>✓</sup> component increases in concentration as a result of evaporation of the solvent to more efficiently remove impurities from the <sup>surface of the</sup> substrate 6 ~~surface~~ and vicinity thereof. This effect <sup>the</sup> of cleaning the substrate <sup>✓</sup> ~~surface~~ exposes the pure substrate <sup>✓</sup> ~~surface~~ <sup>2</sup> to promote physical adhesion between the substrate <sup>✓</sup> ~~surface~~ and polymers <sup>✓</sup> P1 to P4 ~~as the surface modifier~~. At the same time, the acid <sup>✓</sup> ~~component increased in concentration~~ <sup>increase in the acid</sup> <sup>2</sup> as a result of evaporation of the solvent under heating during the drying step for the hydrophilicization treatment solution 8 spread over the substrate 6 surface <sup>2</sup>.

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accelerates partial cleavage of the polymer P1 to P4 ~~as~~  
~~the hydrophilicization agent.~~

FIGS. 4A and 4B schematically illustrates/  
decomposition of the polymer P1 by the concentrated  
5 acid 7. As shown in FIG. 4A, the concentrated acid 7  
acts on the polymer P1, to cleave the main skeleton 1-3  
into the fractionalized products P1a and P1b, as shown  
in FIG. 4B. FIG. 5 illustrates adsorption of the  
fractionalized ~~hydrophilicization~~ agent on the  
10 substrate 6. The main skeleton (having surface energy  
almost equivalent to that of the substrate 6) of the  
fractionalized products of P1a to P4b from the polymer  
P ~~constituting the hydrophilicization agent~~ are  
selectively oriented on the pure <sup>P1a</sup> substrate 6 surface  
15 exposed as a result of the cleaning, as the solvent  
evaporates and the fractionalized products reach a  
saturation concentration in the solution. As a result,  
the group 1-1 (having surface energy different from  
that of the substrate 6) in the surface modifier  
20 outside of the substrate 6 is oriented toward the  
substrate.

Thus, on the surface of the substrate 6 the main  
skeleton of the fractionalized polymers P1a to P4b  
having <sup>the</sup> surface energy almost equivalent to that of the  
25 substrate 6 are oriented <sup>①</sup> and Group 1-1 having <sup>the</sup> surface  
energy different from that of the substrate 6 is  
oriented outward, <sup>i.e.</sup> ~~thus~~ in the opposed <sup>the</sup> direction <sup>from</sup> to the



*the* substrate 6 surface. Therefore, when the group 1-1 is hydrophilic, the substrate ~~6~~ surface becomes hydrophilic and is modified. FIG. 6 schematically illustrates the hydrophilic~~ization~~ agent adsorbed on the substrate surface <sup>9</sup> after the former is spread and dried.

When a specific polymer, e.g., polysiloxane, is used, fractionalized products P1a to P4b are recombined with each other at least partly by condensation, to produce the polymer of higher molecular weight through the bonds (recombination sites C formed by condensation). This can increase <sup>the</sup> strength of the coating film of the hydrophilic~~ization~~ agent. When *a* polysiloxane is used, the siloxane section may be dissociated by the concentrated acid <sup>7</sup> <sub>2</sub> after it is adsorbed by the substrate ~~6~~ <sup>9</sup> surface <sub>2</sub> to be condensed with moisture 11 in air <sup>9</sup> through the recombination sites C, further stabilizing the adsorbed conditions. FIG. 7 schematically illustrates the recombination by condensation of the dissociated siloxane section with moisture 11 in air. The mechanisms involved in the cleavage to form the fractionalized products and their recombination to produce the condensed polymer P1A to P3A are explained below for the case of <sup>using a</sup> polysiloxane as the polymer.

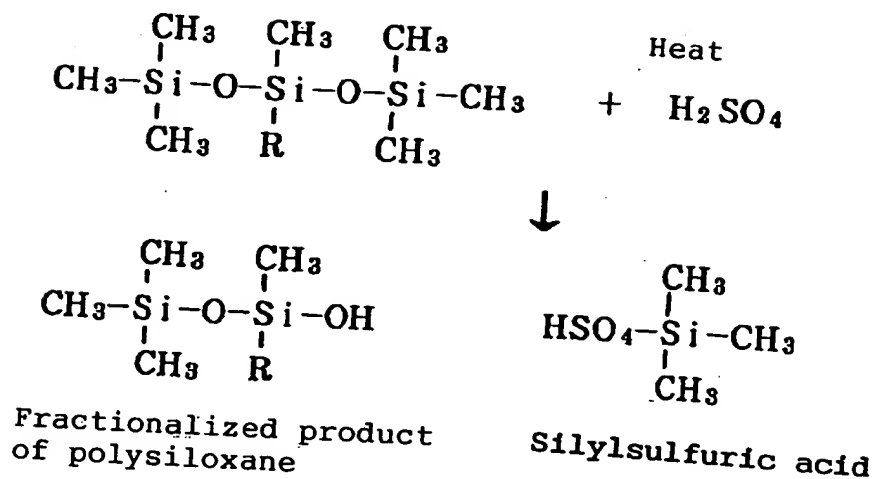
The diluted acid 7 increases in concentration in the surface treatment solution 8 as the solution spread

over the surface to be treated is dried in a controlled manner. The concentrated acid 7 (e.g.,  $H_2SO_4$ ) cleaves the siloxane bond in polysiloxane into the fractionalized polysiloxane products and silylsulfuric acid (Scheme 1). These fractionalized products increase in concentration in the surface treatment solution 8 as the solution ~~spread over the surface to be treated~~ is further dried, increasing <sup>the</sup> probability of contact between them. As a result, the fractionalized products undergo condensation with each other, to reproduce ~~the~~ siloxane bonds (Scheme 2). The methyl group in the silylsulfuric acid as the by-product is oriented toward the surface to be treated, when the surface is hydrophobic, and the sulfone group is oriented in the direction different from that of the surface, conceivably providing some contribution to hydrophilicization of the surface.

↓  
treatment

General formula 1

Scheme 1



Scheme 2

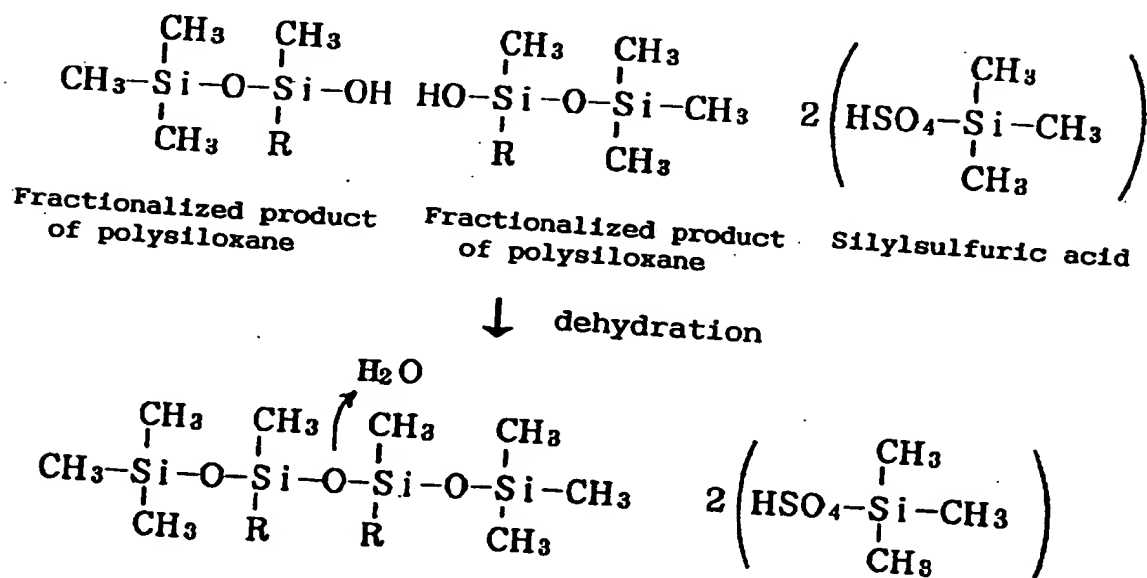


FIG. 8 schematically illustrates one example of *the* conditions of the surface treatment solution *g* when *it there* is ~~of a composition with~~ water (water-containing layer 12) in the solvent. When water is present in the solvent for the treatment solution, which *imparts characteristics onto* hydrophilicizes ~~the~~ the surface under heating, evaporation of the solvent is accompanied by evaporation of water and the volatile organic solvent (10: vapor of volatile organic solvent, and 11: vapor of water). During this step, since the volatile organic solvent is evaporated faster than water, water is concentrated in the solution, to increase surface tension of the solution. This produces a differential surface energy in the interface between the *surface of the* substrate 6 ~~surface to be treated~~ and *the* treatment solution. The section having *the* surface energy almost equivalent to that of the substrate 6 in the fractionalized products Pla to P4b ~~from the polymer as the hydrophilicization agent~~ is oriented toward the substrate *g* ~~surface to be treated~~ in the interface between the substrate *g* ~~surface to be treated~~ and treatment solution whose water content increases as a result of evaporation (water-containing layer 12). At the same time, the section having the hydrophilic group 1-1 in the fractionalized products Pla to P4b ~~from the polymer as the hydrophilicization agent~~ is oriented toward the water-containing layer 12 whose water content increases as a result of evaporation of the

organic solvent. As a result, it is considered that the given orientation of the fractionalized products of the polymer is further improved.

The present invention is applicable to various  
5 elements and purposes, depending on the characteristics and types of the functional groups in the polymers used for surface modification.

(1) When the functional group is hydrophilic

The elements whose surface is modified by the  
10 method of the present invention include water-  
absorptive <sup>elements</sup> ~~ones~~, e.g., paper diapers, sanitary napkins, ink absorbers for ink jet systems, and used ink absorbers (prepared by the method illustrated by one of the preferred embodiment described above, when the  
15 element contains olefin-based fibers), which can be surface-modified by the present invention to be sufficiently hydrophilic to instantaneously absorb liquid. The present invention is also useful for the elements required to hold liquid. The present  
20 invention is also applicable to pigment particles used as an ink colorant. When the particles are surface-modified by the method of the present invention, they may be well-dispersed in water without using a dispersant. The fishery <sup>ing</sup> tools, e.g., fishing nets and  
25 lines, can reach a target point more quickly after ~~being submerged~~ <sup>being submerged</sup> ~~thrown~~ in water <sup>2</sup> when surface-modified by the method of the present invention, because they are more compatible

with water.

(2) When the functional group has affinity for oil

The present invention can impart the required functions to those elements required to have affinity  
5 for oil at the portion in contact with oil, e.g., oil cans and transportation tanks.

(3) When the functional group is liquid-repellent (e.g., hydrophobic group)

The present invention can expand functions of *a*  
10 liquid-repellent liquid (whether it is water or oil) for various elements, e.g., *a* washing stand and kitchen sinks, walls, roads, mirrors, automobile exteriors or the like, and glass surfaces, at the molecular level, or even decrease these functions to desired levels, by  
15 controlling types of the functional groups or their numbers at *a* unit molecule.

(4) When the functional group is polar

The present invention can provide the elements with a filter function (by utilizing anodic properties  
20 for ion-exchanging or removal of impurities), or an adduct function by chemically reacting the element with a certain reactive group. In particular, when the filter composed of a number of fibers is formed by an olefinic polymer, the present invention can provide the  
25 filter with desired characteristics while making it treatable by incineration, and hence, environmentally favorable, as illustrated by one of the preferred

embodiments described above.

The present invention also <sup>provides</sup> gives the element, which  
can develop a color or emit light, when a colorant or  
fluorescent agent reactive with the polar group and  
5 adsorptive is used.

The present invention greatly expands the range of  
these desired characteristics, and can find limitless  
applicable areas.

(5) When the functional group has no characteristics  
10 the element is required to exhibit, but is used to form  
a uniformly thin film

In this case, the functional group is required to  
have interfacial energy different from that of the  
group on the side adsorbed on the polymer surface as  
15 the sole essential condition. It can improve  
orientation of the group to the sections having almost  
equivalent interfacial energy and surface energy. It  
is preferable, in this case, that the polymer is  
cleaved at least partly to cope with more diversified  
20 surface conditions. It is more preferable that the  
fractionalized structure resulting from the cleavage  
(monomer, dimer, trimer or polymer having an  
intermediate molecular weight) is recombined with each  
other by condensation or crosslinking to form a polymer  
25 of higher molecular weight to improve the adhesiveness.

The element provided with these characteristics by  
the present invention for its entire peripheries or

surfaces has the structure surface ~~itself~~ forming the <sup>a</sup>  
strong film, <sup>thus</sup> and <sup>inf</sup> becomes more durable.

(6) The present invention is applicable to any other  
area, so long as the element <sup>1</sup> has improved

5 characteristics <sup>2</sup> by one or more of the mechanisms  
described above. All of these elements are included in  
the present invention.

The present invention provides especially  
excellent effects <sup>2</sup> when it uses a treatment solution  
10 containing a wettability improver capable of improving  
wettability to the element surface and that the solvent  
of the polymer is ~~attainable~~ (e.g., isopropyl alcohol,  
IPA) <sup>can</sup> solvent accelerating <sup>e the</sup> cleavage of the polymer, one  
15 of the functional groups described above, and the  
polymer having interfacial energy different from that  
of the functional group and almost equivalent to  
partial surface energy of the element surface. The  
surface modification, effected by the cleavage and  
subsequent condensation, exhibits particularly  
20 excellent effects <sup>2</sup> and <sup>providing</sup> ~~securely gives~~ uniformity and  
characteristics <sup>that</sup> which cannot be provided by the  
conventional method.

FIG. 23 illustrates one of the process examples  
for producing these elements. This process comprises a  
25 series of steps <sup>2</sup> supply of the element to be treated  
and treatment solution (processing liquid) as the first  
step (S1), application of the treatment solution to the



element surface to be treated (S2), removal of surplus materials from the surface to be treated (S3), concentration/evaporation of the treatment solution for cleavage of the polymer and orientation of the  
5 fractionalized products on the surface to be treated (S4), condensation for recombining the fractionalized products ~~with each other~~ to produce the polymer (S5), and production of the element with modified surfaces (S6).

10 The treatment solution concentration/evaporation step (S4) is preferably effected by a continuous heating/drying step at higher than <sup>the</sup> room temperature but at or lower than <sup>the</sup> boiling point of the solvent (e.g., 60°C) for a varying time, e.g., approximately 45  
15 minutes to 2 hours when polysiloxane having a hydrophilic group is used together with water <sup>and</sup> an acid and organic solvent (e.g., isopropyl alcohol) for modifying the surface composed of a polyolefin-based resin, and around 2 hours when a 40 wt.% aqueous  
20 solution of isopropyl alcohol is used. The drying treatment time may be reduced by decreasing <sup>the</sup> water content.

In the example shown in FIG. 23, the fractionalized products are formed by cleavage of the  
25 polymer on the ~~element~~ <sup>surface</sup> surface to be treated. However, the treatment solution containing the fractionalized products beforehand may be spread over the element

*surface of the*

~~surface to be treated~~<sup>be ed</sup> to orient ~~them~~ thereon.

As described above, the treatment solution composition useful for the present invention comprises, e.g., a wettability improver, which <sup>is</sup> has <sup>le to</sup> wettability with the surface to be modified, for making the treatment solution more wettable <sup>to</sup> with the surface to be treated and, at the same time, works <sup>my</sup> as a good solvent for the surface modifier; solvent; polymer-cleaving catalyst; and polymer <sup>that</sup> which contains a functional group for imparting the modification <sup>effects on to</sup> ~~effect~~ to the surface ~~to be~~ modified and another group for imparting adhesive function to the surface ~~to be modified~~. <sup>don</sup>

#### Examples

The surface modification method of the present invention, element surface modified by the method, and evaluation thereof are described more <sup>specially</sup> ~~concretely~~ by the Examples. It is to be understood that <sup>the</sup> Examples are to provide some of the preferred embodiments and not to limit the present invention.

#### Example 1

This example applied the present invention to modification of the internal hydrophobic wall surfaces of a polypropylene container 90 to <sup>make them</sup> ~~be~~ hydrophilic, as illustrated in FIG. 9A.

The hydrophilicization treatment solution having a composition given in Table 1 was prepared.

g g  
[Table 1]

(Hydrophilicization treatment solution composition)

Components	Contents (wt.%)
Polyoxyalkylene-poly(dimethyl siloxane)	4.0
Sulfuric acid	0.5
Isopropyl alcohol	95.5

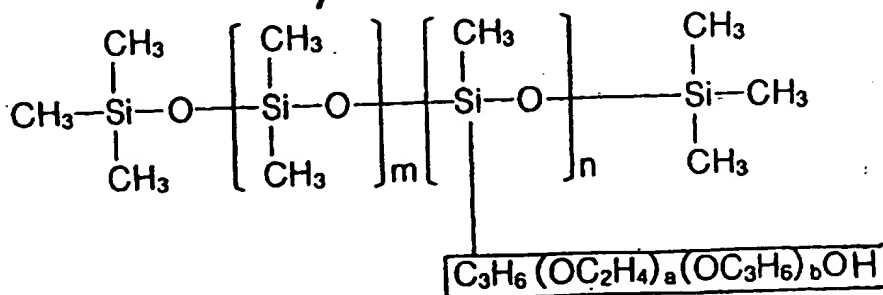
The solution was prepared using isopropyl alcohol as an organic solvent alcohol, <sup>which is a good solvent for</sup> well dissolving polyoxyalkylene-poly(dimethyl siloxane) ~~as the polymer~~.

Isopropyl alcohol was first well mixed with sulfuric acid, <sup>which is used</sup> as an inorganic acid, added to 0.5 wt.% ~~as to increase the concentrated sulfuric acid~~ concentration in the final solution. Then, polyoxyalkylene-poly(dimethyl siloxane) ~~as the polymer~~ was added to the above mixture to 4.0 wt.%, as polymer concentration in the final solution, and uniformly dissolved therein, to prepare the hydrophilicization treatment solution.

Polyoxyalkylene-poly(dimethyl siloxane) used for

Example 1 is shown by the general formula (1):

[General formula 2]



where, (m) and (n) are each a positive integer; (a) and

(b) are also each a positive integer; and R is an alkyl or hydrogen. The polymer has a structure of poly(dimethyl siloxane) with one of the methyl groups in the main repeating unit being substituted by a polyoxyalkylene group. The commercial product (Nippon Unicar, silwet L-7002™) was used. The section enclosed by a rectangle in the general formula (1) is a hydrophilic group, which corresponds to the first group (functional group) in FIGS. 1A and 1B and group 1-1 in FIG. 24.

The above treatment solution dissolves a small quantity of water molecules, associated with concentrated sulfuric acid, in addition to the sulfuric acid molecules.

The treatment was attempted to make hydrophilic the inner wall surfaces of a polypropylene (PP) container 40 shown in FIG. 9A with the above hydrophilicization treatment solution. A small quantity of the hydrophilicization treatment solution prepared was put in the PP container of 50 ml in inner volume, to wet the container inner surfaces with the hydrophilicization treatment solution. The container was turned upside down and shaken, after the inner surfaces were uniformly wetted, to release the surplus solution. The container whose inner surfaces were wetted with the coating film 48 of the hydrophilicization treatment solution was dried in an

oven at 60°C for 1 hour. This produced the hydrophilic<sup>ally</sup>ization-treated PP container 40A, shown in FIG. 9B.

9/ Comparative Examples 1 to 3/

5        The ~~three~~ types of solutions having the following compositions were prepared, ~~and~~ <sup>2</sup> the treatment was attempted for the inner wall surfaces of a polypropylene (PP) container with each of these solutions, <sup>2</sup> to verify the hydrophilic<sup>imparted</sup>ization treatment effects ~~brought~~ <sup>imparted</sup> by the present invention.

10

(1) Solution composition for Comparative Example 1

Comparative Example 1 used the hydrophilic~~ization~~-treatment solution composition shown in Table 1, except that it comprised only isopropyl alcohol and sulfuric acid. In other words, the solution for Comparative Example 1 was free of polyoxyalkylene-poly(dimethyl siloxane), which was used to form the desired polymer coating film by the present invention.

15

(2) Solution composition for Comparative Example 2

20        Comparative Example 2 used the hydrophilic~~ization~~-treatment solution composition shown in Table 1, except that it comprised only isopropyl alcohol and polyoxyalkylene-poly(dimethyl siloxane). In other words, the solution for Comparative Example 2 was free of concentrated sulfuric acid and a small quantity of the water molecules associated therewith.

25

(3) Solution composition for Comparative Example 3

Comparative Example 3 used the hydrophilicization-treatment solution composition shown in Table 1, except that isopropyl alcohol was replaced by hexane, which is a bad solvent for polyoxyalkylene-poly(dimethyl siloxane).

A small quantity of each of the above solutions was put in the PP container of 50 ml in inner volume, to wet the container inner surfaces in a manner similar to that <sup>in</sup> ~~for~~ Example 1. Each container was turned upside down and shaken, after the inner surfaces were uniformly wetted, to release the surplus solution. The container whose inner surfaces were wetted was dried in an oven at 60°C for 1 hour. The untreated PP container was also used in <sup>the</sup> Reference Example.

Each PP container was evaluated whether its <sup>to determine</sup> ~~conditions were satisfactory or not.~~ <sup>was obtained</sup> <sup>or not a satisfactory</sup> treated surface ~~conditions were satisfactory or not.~~ The evaluation methods and results are described below.  
a) Method for evaluating hydrophilicity <sup>properties</sup> of the PP container

The inner surfaces of a total of 4 PP containers, treated with the solution <sup>of</sup> ~~for~~ Example 1 or Comparative Examples 1, 2 or 3, and the untreated <sup>container</sup> ~~one~~ (Reference Example) were rinsed with pure water. Each container was filled with fresh pure water to approximately one-third of the inner volume, after rinse water was discarded, and lightly shaken, to visually confirm conditions of pure water attaching to the inner wall

surfaces<sup>(5)</sup> of the container<sup>(A)</sup>

b) Evaluation results of hydrophilicity of the PP container

The inner surface of the PP container  
5 hydrophilization<sup>also</sup>, treated in Example 1 was wetted with  
pure water, <sup>compared to</sup> ~~with the conditions of~~ the untreated PP  
container for Reference Example, <sup>which was used</sup> ~~as the~~ reference. By  
contrast, those of the PP containers treated with the  
solution prepared <sup>in</sup> ~~by~~ Comparative Example 1, 2 or 3 were  
10 not wetted at all, because pure water was observed to  
trickle down in droplets. ~~o~~

<sup>these containers</sup> Each of ~~them~~ clearly had the hydrophobic inner  
surface, as was the case with the <sup>reference container</sup> ~~one for Reference~~  
Example.

15 The solutions for Comparative Examples 2 and 3  
contained polyoxyalkylene-poly(dimethyl siloxane),  
which, however, was not effectively adsorbed by the PP  
surfaces. As a result, it was washed off when the  
treated containers were rinsed with pure water  
20 immediately before they were evaluated.

By contrast, the PP container treated in Example 1  
was wetted with pure water after it was rinsed ~~with~~  
~~pure water~~, indicating that polyoxyalkylene-  
poly(dimethyl siloxane) ~~was fast adsorbed~~ by the PP  
25 surface ~~and it was~~ effectively adsorbed.

These evaluation results indicate that the surface  
of plastic material can be effectively

hydrophilicization<sup>ally</sup> treated with a solution containing a polyalkylsiloxane having a polyalkyleneoxide chain, acid and alcohol, <sup>which is</sup> spread over the PP container and dried. It <sup>was</sup> found that a polymer ~~of~~ polyalkylsiloxane

5 can be oriented on and attached to the PP surface as ~~desired~~ <sup>aimed</sup> when the surface is treated with the polymer in the presence of <sup>an</sup> the alcohol and <sup>an</sup> acid. It ~~is also~~ <sup>was</sup> confirmed that a combination of the acid and alcohol also ~~has an effect of cleaning~~ <sup>S</sup> the plastic surface, and  
10 that the cleaned surface coupled with the methyl group in the alkylsiloxane structure (as the repeating unit of the hydrophobic polyalkylsiloxane having a polyalkyleneoxide chain) oriented on the substrate surface improves overall adhesive power.

15 The polyalkylsiloxane having a polyalkyleneoxide chain can be uniformly dispersed on and effectively attached to the plastic surface, because it is dissolved in the alcohol, <sup>which is</sup> as a good solvent <sup>for this polymer</sup> therefor. When a hydrophilic surfactant only is spread over the  
20 plastic surface and dried thereon, the surface shows <sup>characteristics</sup> hydrophilicity only during the initial stage, which, however, <sup>are</sup> ~~is~~ lost when the surface is rinsed with pure water, because the surfactant is dissolved <sup>in</sup> and ~~eluted~~ <sup>removed by</sup>  
~~out in~~ water.

25 Example 2

Example 2 applied the surface modification method of the present invention to a fibrous element, more



~~specifically~~  
concretely to an element of polypropylene/polyethylene  
to conduct a  
(PP/PE) fibers for surface hydrophilicization  
treatment. The element of PP/PE fibers actually  
prepared was a block-shaped one in which the fibers  
5 were composited with each other to take a form useful  
for, e.g., an ink absorbing element, which could absorb  
liquid (e.g., ink) and hold the used liquid. For  
example, referring to FIG. 10A, a container 21 having  
an adequate shape and open to air by an opening 25 can  
10 be used as a liquid-holding container 20, when it is  
filled with fibrous bodies 23, capable of functioning  
as an absorbing element 24 to absorb and hold various  
types of liquid (e.g., ink), oriented in a given  
direction. Such an ink-absorbing element 24 can be  
15 suitably used for a discharged ink tank for ink jet  
recorders.

More ~~concretely~~ <sup>specifically</sup>, the fibrous element 23, which  
constituted the absorbing element 24, was composed of  
the biaxial fibrous element of polypropylene and  
20 polyethylene fibers, each approximately 60 mm long.  
This biaxial fibrous element was of a core-sheath  
structure, with a polypropylene fiber having a higher  
melting point as the core 23b encased by polyethylene  
having a lower melting point as the sheath 23a. FIG.  
25 11A shows its section perpendicular to the axial  
direction, whose external shape (outer peripheral  
shape) was essentially circular (closed ring shape).

The fibrous blocks, each composed of the short fibers and having the above section, were arranged in the fiber axis direction in, and heated by, a cotton-carding machine, to fuse the fibers with each other.

5 More <sup>specifically</sup> ~~concretely~~, they were heated at above melting point of polyethylene as the sheath 23a but below melting point of polypropylene as the core 23b, to <sup>obtain a</sup> ~~have~~ the structure with the sheaths 23a <sup>of</sup> polyethylene <sup>ed with</sup> fusing each other at their points, ~~they came into contact~~ <sup>of</sup> ~~with each other.~~

10

In the above fibrous structure 23, referring to FIG. 10B, the fibers 23A were arranged in the fiber axis direction in the cotton-carding machine and continuously arranged mainly in the longitudinal

15 direction (F1). They came into contact with, or close to, each other at points, e.g.,  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\epsilon$ , ~~as~~ shown in FIG. 10C. They were fused with each other under heating at the contact (intersection) points, e.g., at the points  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\epsilon$ , as shown in FIG. 10D, to form

20 a network structure, giving the structure mechanical elasticity in the direction F2 perpendicular to the longitudinal direction F1. This was accompanied by increased <sup>the</sup> tensile strength in the longitudinal direction F1 shown in FIG. 10B. The structure,

25 although lower in tensile strength in the direction F2 than in F1, was elastic with <sup>an</sup> ~~restoring~~ force against compressive stress in the direction F2.

Looking<sup>at</sup> the fibrous structure 23 in more detail,  
referring to FIG. 10D, the individual fibers 23A were  
crimped, to help form complex network structures  
between the adjacent fibers, and fused with each other,  
5 e.g., at the points  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\epsilon$ . Some of the crimped  
fibers 23A were arranged in the direction F2  
perpendicular to the longitudinal direction F1, to make  
the structure three-dimensional with the fibers fused  
with each other. The fibrous element 23 actually  
10 prepared in Example 2 was formed into a concentric  
sliver of biaxial fiber tows, shown in FIG. 11A, with a  
polypropylene fiber (melting point: around 180°C) as  
the core 23a encased in polyethylene (melting point:  
around 132°C). The fibrous element 23, composed of the  
15 fibers mainly oriented in the longitudinal direction  
F1, shows fluid conditions within the element and  
stationary liquid-holding conditions clearly different  
in the directions F1 and F2, when immersed in a liquid.

In this example, the element shape was of a  
20 fibrous structure, generally holding more liquid than  
the container with planar surfaces, e.g., <sup>the container</sup> that prepared  
by Example 1, and the treatment solution of the  
following composition was used:

g Table 2

g Hydrophilicization treatment solution composition of fiber

Components	Composition (wt.%)
Polyoxyalkylene-poly(dimethyl siloxane)	0.40
Sulfuric acid	0.05
Isopropyl alcohol	99.55

(1) Method for<sup>a</sup> hydrophilicization~~ization~~ treatment of the absorption body of PP/PE fibers

The absorption body 24 of polypropylene/polyethylene fibers, having the fusion-treated structure shown in FIG. 12A, was immersed in the hydrophobicization~~ization~~ treatment solution 28 of the above composition (FIG. 12B). The solution 28 was held in the voids between the fibers 23A for the fibrous absorption body 24, as shown in FIG. 12E as the magnified view of FIG. 12B. The fibrous absorption body 24 holding the solution 28 was pressed by a pressing jig 27, e.g., metallic mesh (FIG. 12C), to remove the surplus treatment solution 28 held in the voids between the fibers 23A, as shown in FIG. 12F as the magnified view of FIG. 12C. When the jig 27 was removed, the fibrous absorption body 24 returned back to the original shape, as shown in FIG. 13A, with the fibers 23A coated with the liquid layer 28A. The absorption body 24 with the fibers wetted with the

solution was dried in an oven 29 at 60°C for 1 hour  
(FIG. 13B). This produced the fibrous absorption body  
24 with the fibers 23A coated with the hydrophilic  
layer 28B, as shown in FIG. 13C. FIGS. 12D to 12F are  
5 partially magnified views of respective FIGS. 12A to  
12C, and FIGS. 13D to 13F are partially magnified views  
of respective FIGS. 13A to 13C.

~~Comparative Example 4 and Reference Example 1~~

In Comparative Example 4, the fibrous absorption  
10 body was hydrophilicization<sup>ally</sup> treated in the same manner  
as in Example 2 except that the treatment solution  
comprised only sulfuric acid and isopropyl alcohol. In  
other words, the solution for Comparative Example 4 was  
free of polyoxyalkylene-poly(dimethyl siloxane). The  
15 untreated fibrous absorption body of PP/PE fibers was  
also used in Reference Example 1.

In Example 2, 0.5 g of the fibrous absorption body  
of PP/PE fibers was treated by the above-described  
treatment method with 0.3 to 0.5 g of the above  
20 hydrophilicization<sup>ally</sup> treatment solution. Comparative  
Example 4 used the same quantity of the solution  
applied to the whole element using the above-described  
application method.

Each fibrous absorption body thus prepared was  
25 evaluated <sup>to determine - satisfactory</sup> whether ~~its treated~~ surface conditions were <sup>achieved</sup>  
~~satisfactory or not~~. The evaluation methods and  
results are described below.

(1) Method for evaluating hydrophilicity<sup>properties</sup> of the fibrous absorption body of PP/PE fibers

a) Evaluation by pure water drops <sup>deposited by</sup> ~~fallen~~ from a dropper

Pure water drops were <sup>released</sup> ~~fallen~~ from a dropper onto

5 the fibrous absorption bodies of PP/PE fibers, prepared by Example 2 and Comparative Examples 4, and the untreated <sup>body</sup> ~~one~~ (Reference Example), to observe <sup>the</sup> extent of pure water sinking into the bodies.

b) Evaluation by immersion in pure water

10 The fibrous absorption bodies of PP/PE fibers, prepared by Example 2 and Comparative Examples 4, and the untreated <sup>body</sup> ~~one~~ (Reference Example), were slowly placed on pure water, held by a container sufficiently large to accommodate the fibrous element, to observe <sup>the</sup> extent of pure water sinking into the bodies.

15 (2) Results of evaluation of hydrophilicity<sup>properties</sup> of the fibrous absorption body of PP/PE fibers

(a) Results of evaluation by pure water drops <sup>deposited by</sup> ~~fallen~~ from a dropper

20 Pure water drops, <sup>released</sup> ~~fallen~~ from a dropper onto the fibrous absorption body of PP/PE fibers prepared by Example 2, were observed to instantaneously sink into the element ~~inside~~.

By contrast, pure water drops <sup>released</sup> ~~fallen~~ from a dropper onto the fibrous absorption body of PP/PE fibers prepared by Comparative Example 4 and <sup>the</sup> untreated <sup>body</sup> ~~one~~ (Reference Example 1) were observed not to sink

into the element <sup>①</sup> ~~inside~~ <sup>The drops were</sup> ~~but~~ repelled to form droplets on the surfaces.

b) Results of evaluation by immersion in pure water

The fibrous absorption body prepared by Example 2  
5 was slowly placed on pure water held by a container,  
and observed to slowly sink into water, indicating that  
its surfaces were hydrophilic.

By contrast, both the fibrous absorption body of  
PP/PE fibers prepared by Comparative Example 4 and <sup>the</sup>  
10 untreated <sup>body</sup> ~~one~~ (Reference Example 1) <sup>2</sup> slowly placed on  
pure water held by a container <sup>2</sup> were observed to  
securely float on water. They showed no sign <sup>of</sup> ~~to~~ absorbing  
water thereafter, indicating that they were clearly  
hydrophobic.

15 These results indicate that the fibrous absorption  
body of PP/PE fibers can be also coated with a  
polyalkyl siloxane layer (hydrophilic layer) 28B, as  
shown in FIG. 13C, to be effectively  
hydrophilic <sup>ally</sup> ~~ization~~ <sup>2</sup> treated, when the solution  
20 containing a polyalkyl siloxane having a polyalkylene  
oxide chain, acid and alcohol was spread over the  
element surface and dried. Therefore, it <sup>was</sup> ~~is~~ found that  
the fibrous absorption body 24 of PP/PE fibers can ~~have~~  
~~a~~ sufficient <sup>ally</sup> ~~function~~ ~~to serve~~ as an element <sup>of</sup> ~~for~~  
25 absorbing aqueous ink.

The fiber surfaces were analyzed by a scanning  
electron microscope (SEM) <sup>2</sup> in order to verify that the

surface modification method of the present invention attaches a polyalkyl siloxane having a polyalkylene oxide chain to the PP/PE fiber surface to form the polymer coating layer thereon.

5           FIGS. 14, 15 and 16 show the magnified SEM photographs of the untreated PP/PE fiber surfaces of the fibrous absorption body of Reference Example 1 (magnification: 150, 500 and 2,000, respectively). FIG. 17 shows the magnified SEM photograph of the PP/PE  
10 fiber surfaces of the fibrous absorption body of Comparative Example 4, treated with only the acid and alcohol (magnification: 150).

          FIGS. 18, 19 and 20 show the magnified SEM photographs of the PP/PE fiber surfaces of the  
15 hydrophilic<sup>ally</sup>ization-treated fibrous absorption body of Example 2 (magnification: 150, 500 and 2,000, respectively).

          No structural changes<sup>were</sup> considered to result from deposition<sup>ng. An</sup> of organic substance on the fiber surfaces, <sup>as</sup>  
20 ~~are~~ clearly shown in all of these magnified SEM photographs of the PP/PE fiber surfaces. Indeed, no difference is observed between the untreated PP/PE fiber surfaces (FIG. 16) and hydrophilic<sup>ally</sup>ization-treated PP/PE fiber surfaces (FIG. 20) even <sup>if magnified by a factor of 2</sup> by the 2000 times  
25 ~~magnified SEM photographs~~. It is therefore judged that the hydrophilic<sup>ally</sup>ization-treated PP/PE fibers are uniformly coated with a thin film (considered to be



monomolecular layer) of polyoxyalkylene-poly(dimethyl siloxane) <sup>and their</sup> showing appearances <sup>is</sup> not differentiated from the untreated surfaces <sup>when evaluated via</sup> by the SEM analysis.

By contrast, the PP/PE fiber surfaces treated only  
5 with the acid and alcohol show the fiber intersections  
(fused sections) cut at many points and <sup>also have</sup> many knot-like  
sections in the fibers, as shown in the SEM photograph  
(FIG. 17). These changes are considered to result from  
deterioration of the PE/PP molecules on the fiber  
10 surfaces (in particular PE molecules in the surface  
layer) during the heating/drying step, accelerated by <sup>the</sup>  
increased concentration of the acid as a result of  
evaporation of the solvent and heat <sup>used</sup> ~~itself~~ for the  
drying step.

15 On the other hand, the hydrophilicization ~~treatment~~  
treatment <sup>of</sup> for the present invention <sup>does not</sup> causes ~~no~~ cutting  
at the fiber joints <sup>Y</sup> nor formation of knot-like sections  
in the fibers, which are observed in the PP/PE fiber  
surfaces treated only with the acid and alcohol,  
20 <sup>even when</sup> ~~although it uses~~ the treatment solution containing <sup>S</sup> the  
same concentration of the acid and the same  
heating/drying step. <sup>is performed</sup> This fact indicates <sup>A</sup> controlled  
deterioration of the PE molecules on the fiber surfaces  
during the hydrophilicization ~~treatment~~ <sup>2</sup> for Example 2.  
25 It is considered, even when the acid acts on the fiber  
surfaces to cut the PE molecules and produce radicals  
within the molecules, that some materials and

structures capture the radicals to control <sup>the</sup> destruction of the PE molecules by ~~the~~ chain reactions caused by the radicals. It cannot be ruled out that polyoxyalkylene-poly(dimethyl siloxane) attaching to the fiber surfaces is involved in the capture of the radicals to form the chemical bonds with the PE surfaces while capturing the radicals formed and thereby ~~to control~~ <sup>the</sup> destruction of the PE/PP molecules by the radical-caused chain reactions.

Overall, it is judged that modification of the fiber surfaces is achieved in Example 2 by the thin film of polyoxyalkylene-poly(dimethyl siloxane) uniformly deposited on the fiber surfaces. The favorable side <sup>effects</sup> during the hydrophilicization treatment include cleaning of the fiber surfaces by the acid and solvent contained in the treatment solution, which possibly accelerates physical adsorption of the polyalkylene oxide chain. The chemical bonding between the PE molecules, cut by the acid of increased concentration and heat, and polyalkylene oxide chains can occur <sup>on a large scale</sup> ~~to no small extent~~.

The biaxial fiber may be eccentric, as shown in FIG. 11B, with the core section (core material) 23b partly exposed to the outer surface, as a result of which the fiber surfaces have the outer layer (sheath) 23a surfaces and core surfaces. The surface modification method of the present invention can impart

*properties*  
 hydrophilicity to both the exposed core surfaces and sheath surfaces, even in such a case. When a hydrophilic surfactant only is spread over the surface and dried thereon, the surface partly shows hydrophilicity <sup>*properties*</sup> only during the initial stage, <sup>*These properties are,*</sup> ~~which~~ however, ~~is~~ lost when the surface is rinsed with pure water with lightly rubbing, because the surfactant is ~~seen~~ <sup>*in removed by*</sup> dissolved and ~~eluted out in~~ water.

*Example 3*

10 This example applied the present invention to a hydrophilicization treatment of plastic particle surfaces. More <sup>*specifically*</sup> ~~concretely~~, the polypropylene particle surfaces were treated in a manner similar to that ~~for~~ <sup>*in*</sup> Example 1, which modified the water-repellent inner wall surfaces of the polypropylene container to be hydrophilic.

The hydrophilicization treatment solution having a composition ~~given~~ in Table 3 was prepared.

*Table 3* *shown*

~~Hydrophilicization~~ treatment solution composition

Components	Composition (wt.%)
Polyoxyalkylene-poly(dimethyl siloxane)	4.0
Sulfuric acid	0.5
Isopropyl alcohol	95.5

The solution was prepared by the method similar to that <sup>in</sup> for Example 1. Isopropyl alcohol was first well mixed with sulfuric acid added to 0.5 wt.%, ~~as concentrated sulfuric acid~~ concentration in the final solution. Then, polyoxyalkylene-poly(dimethyl siloxane) was added to the above mixture to 4.0 wt.%, <sup>as a</sup> polymer concentration, in the final solution, and uniformly dissolved therein, to prepare the above hydrophilicization ~~treatment~~.

10 (1) Hydrophilicization <sup>2</sup> treatment of polypropylene (PP) particles

The PP particles 31 used for Example 3 were spherical, having a diameter of 2 mm.

15 The PP particles 31 were immersed in the above hydrophilicization <sup>2</sup> treatment solution 38, and then scooped up to be separated from the solution. The PP particles 31 coated with the treatment solution 38 were put in a container 30 (FIG. 22), <sup>2</sup> and <sup>1</sup> hot wind was vigorously sent into the container 30, <sup>2</sup> while stirring and <sup>11</sup> the particles 31 <sup>11</sup> were stirred to prevent fusing ~~these particles with each other~~. These particles were treated during this step by evaporating the solvent included in the treatment solution 38 and drying the particles. This treatment method is one of the preferred embodiments of the present invention, because of <sup>its</sup> the favorable effects ~~it brings~~; e.g., uniform coating and film-making resulting from rotation of the PP particles ~~themselves~~.

<sup>1</sup> the

and surface tension around the spheres<sub>2</sub> to secure<sup>a</sup> uniform coating.

(Reference Example 2)

5 The untreated PP particles were used for Reference Example 2.

The treated surface conditions were evaluated by the following methods for the PP particles treated for surface modification (Example 3) and untreated (Reference Example 2).

10 Method for evaluating hydrophilicity<sup>properties</sup> of the PP particles

(1) Evaluation by stirring with pure water

The PP particles, hydrophilicization<sup>ally</sup> treated for surface modification (Example 3) and untreated (Reference Example 2)<sub>2</sub> were put in pure water held in a polyethylene container and stirred therein by a stirrer<sub>2</sub> to observe the particle conditions.

(2) Evaluation results of hydrophilicity<sup>properties</sup> of the PP particles

20 The results of evaluation by stirring with pure water are described. When the PP particles treated in (Example 3)<sub>2</sub> were stirred in pure water, they were found to be dispersed and stirred in pure water. By contrast, the untreated PP particles (Reference Example 2) were scarcely dispersed in pure water<sup>more</sup> and found to be forced to move toward the polyethylene container walls and float on pure water.

The results indicate that the PP particles prepared by Example 3 were well <sup>hydrophilically</sup> surface-treated for ~~hydrophilicization~~, as was the case with the container prepared by Example 1. This means that the untreated

5 PP particle surfaces (shown in FIG. 21A) were densely coated with the coating film 38A of polyoxyalkylene-poly(dimethyl siloxane), as shown in FIG. 21B. It ~~is~~ <sup>was</sup> also confirmed that the method of the present invention is applicable not only to a flat plane (Example 1) but

10 also to a curved surface, such as particle surface (Example 3), to easily form the polymer coating 38A as schematically shown in FIG. 21D. As shown, the ring-shaped polymer coating 38A on the surface periphery (closed ring-shaped section of the section periphery)

15 ~~to keep~~ the surface-modified section <sup>from easily</sup> ~~not~~ coming off easily. FIG. 21A is the section of the untreated PP particle, FIGS. 21B and 21C are the section of the <sup>ally</sup> hydrophilicization-treated PP particle and its partially magnified view, respectively, and FIG. 21D is

20 the polymer film covering the outer periphery of the PP particle.

~~Example 4~~

Example 4 applied the method of the present invention to a fibrous element of

25 propylene/polyethylene (PP/PE) fibers for surface modification with a solution containing poly(dimethyl siloxane) (amino-modified poly(dimethyl siloxane))

having amino group as the functional group.

More <sup>specifically</sup> ~~concretely~~, the fibrous element of PP/PE fibers was coated with amino-modified poly(dimethyl siloxane) <sub>3</sub> by the procedure similar to that <sup>in</sup> ~~for~~ Example 2, to modify the water-repellent polypropylene surface to be hydrophilic. The fibrous element of PP/PE fibers used in this example was the same as the one <sup>in</sup> ~~for~~ Example 2.

This example used the same hydrophilicization treatment solution as that <sup>in</sup> ~~for~~ Example 2, except that polyoxyalkylene-poly(dimethyl siloxane) was replaced by amino-modified poly(dimethyl siloxane).

Table 4

(Surface modification solution composition)

Components	Composition (wt.%)
Amino-modified poly(dimethyl siloxane)	0.4
Sulfuric acid	0.05
Isopropyl alcohol	95.55

The solution was prepared using isopropyl alcohol as an organic solvent alcohol well dissolving amino-modified poly(dimethyl siloxane) as the polymer. The amino-modified poly(dimethyl siloxane) used had a structure with one of <sup>the</sup> ~~the~~ methyl groups in the repeating unit of poly(dimethyl siloxane) substituted by a functional group having <sup>an</sup> ~~a~~ amino group. It was a commercial product (GE Toshiba Silicone, modified

silicone oil TSF47003).

Isopropyl alcohol was first well mixed with amino-modified poly(dimethyl siloxane) added to 0.4 wt.%, as polymer concentration, in the final solution. Then, 5 sulfuric acid as an inorganic acid was added to the above mixture to <sup>a concentration of</sup> 0.05 wt.%, ~~as concentrated sulfuric acid concentration~~ in the final solution, and uniformly dissolved therein, to prepare the surface modification solution.

10 (1) Method for surface treatment of the fibrous absorption body of PP/PE fibers

The absorption body of polypropylene/polyethylene fibers, having the structure shown in FIG. 12A, was immersed in the hydrophobicization<sup>2</sup> treatment solution 15 28 of the above composition (FIG. 12B). The solution was held in the voids between the fibrous absorption body. The fibrous absorption body holding the solution was pressed (FIG. 12C) <sup>2</sup> to remove the surplus treatment solution held in the voids between the fibers. When 20 the pressing jig, e.g., metallic mesh, was removed, the fibrous absorption body returned back to the original shape, as shown in FIG. 13A, with the fibers coated with the liquid layer. The absorption body with the fibers wetted with the solution was dried in an oven at 25 60°C for 1 hour (FIG. 13B).



~~Reference Example 3~~

The untreated fibrous absorption body of PP/PE fibers was used for Reference Example 3.

Each fibrous absorption body of PP/PE fibers thus prepared was evaluated <sup>to determine</sup> whether ~~its treated~~ <sup>unsatisfactory</sup> surface conditions were ~~satisfactory~~ <sup>achieved</sup> or not.

(1) Method for evaluating surface modification of the fibrous absorption body of PP/PE fibers

a) Evaluation by immersion in an aqueous solution of <sup>an</sup> anionic dye

The fibrous absorption bodies of PP/PE fibers, prepared by Example 4 and <sup>an</sup> ~~untreated one~~ <sup>body</sup> (Reference Example 3), were immersed in a 10% aqueous solution of C.I. Direct Blue 199 dye as the anionic dye, and then washed with pure water with rubbing <sup>2</sup> to observe the washed conditions.

b) Results of evaluation of the surface modification of the fibrous absorption body of PP/PE fibers

The following results were obtained by the evaluation tests by immersion in an aqueous solution of <sup>an</sup> anionic dye.

The fibrous absorption body of PP/PE fibers prepared by Example 4 remained lightly cyan in color derived from the dye <sup>2</sup> when immersed in a 10% aqueous solution of C.I. Direct Blue 199 dye, <sup>deriving</sup> as the anionic dye, and then washed with pure water with rubbing.

By contrast, the untreated fibrous absorption body

of PP/PE fibers for Reference Example 3 returned back to the original color of white, when immersed in a 10% aqueous solution of C.I. Direct Blue 199 dye as ~~the anionic dye~~ and then washed with pure water with rubbing, indicating that the aqueous dye solution was washed off and that <sup>the body</sup> it was not compatible with the solution.

As described above, the fibrous absorption body of PP/PE fibers prepared by Example 4, where it was surface-modified with poly(dimethyl siloxane) having an amino group as the functional group, remained lightly cyan in color, when immersed in the aqueous dye solution and then washed with water, indicating that the amino-modified poly(dimethyl siloxane) attached to the surfaces of the fibrous absorption body of PP/PE fibers, <sup>because a</sup> ~~when the~~ solution containing the amino-modified poly(dimethyl siloxane), acid and alcohol was spread over the surface and dried. In other words, the fibrous absorption body of PP/PE fibers was coated with the amino-modified poly(dimethyl siloxane), and surface-modified into the cationic element by the amino group as a cationic group in the amino-modified poly(dimethyl siloxane). The fibrous absorption body of PP/PE fibers, becoming cationic by the surface modification, reacted with the anionic dye in the aqueous anionic dye solution, <sup>and was</sup> ~~to be~~ colored. It was also found that the fibers were ~~colored cyan~~ inside, <sup>cyan-colored</sup> ~~by~~

on the

which was indicated that the surface modification method of the present invention effectively modified <sup>the</sup> inside of the fiber assembly of <sup>a</sup> complex structure.

In Example 4, amino-modified poly(dimethyl siloxane) having <sup>an</sup> amino group as a cationic functional group was used for modification of the water-repellent PP surface. However, it is considered that the PP surface can be surface-modified to be anionic, <sup>2</sup> when a functional group other than a cationic <sup>group</sup> ~~one~~, e.g., anionic functional group, is used as the functional substituent for the poly(dimethyl siloxane) section as the skeleton of amino-modified poly(dimethyl siloxane). An anionic functional group may be used together with an alkali substance as the cleavage catalyst. Thus, it is considered that PP can be surface-modified to have desired properties for specific purposes by changing the functional substituent for the poly(dimethyl siloxane) section as the skeleton to be utilized for the surface deposition, depending on surface modification purposes.

#### <sup>9</sup> Example 5 <sup>9</sup>

This example applied the present invention to a surface modification of plastic particle surfaces with a solution containing <sup>an</sup> amino-modified poly(dimethyl siloxane). More <sup>specifically</sup> ~~concretely~~, the polypropylene particle surfaces were coated, in a manner similar to that ~~for in~~ Example 3, with amino-modified poly(dimethyl siloxane)

<sup>1</sup>  
*the*

~~for surface modification of the water-repellent  
polypropylene surface.~~

The hydrophilicization treatment solution having a composition <sup>shown</sup> ~~given~~ in Table 5 was prepared.

Table 5

(Hydrophilicization treatment solution composition)

Components	Composition (wt.%)
Amino-modified poly(dimethyl siloxane)	0.4
Sulfuric acid	0.05
Isopropyl alcohol	95.55

The solution was prepared by the method similar to that ~~for~~ <sup>in</sup> Example 4. Isopropyl alcohol was first well mixed with <sup>the</sup> amino-modified poly(dimethyl siloxane) added to <sup>a concentration of</sup> 0.4 wt.% ~~as polymer concentration~~ in the final solution. Then, sulfuric acid ~~as an inorganic acid~~ was added to the above mixture to <sup>a concentration of</sup> 0.05 wt.% ~~as concentrated sulfuric acid concentration~~ in the final solution, and ~~was~~ uniformly dissolved therein, to prepare the surface modification solution.

(1) Surface modification of polypropylene (PP) particles

The PP particles used for Example 5 were spherical, having a diameter of 2 mm.

The PP particles were immersed in the above surface modification solution, and then scooped up to be separated from the solution. The PP particles

coated with the treatment solution were put in a container 30 (FIG. 22), and hot wind was vigorously sent into the container, while ~~stirring~~ the particles *were stirred* to prevent fusing ~~these particles with each other~~, in a manner similar to that <sup>in</sup> ~~for~~ Example 3. These particles were treated during this step by evaporating the solvent and drying the particles.

*(Reference Example 4)*

The untreated PP particles were used for Reference Example 4.

The treated surface conditions were evaluated by the following methods for the PP particles treated for surface modification (Example 5) and untreated *particles* (Reference Example 4).

(1) Method for evaluating surface modification of the PP particles

a) Evaluation by immersion in an aqueous solution of *an* anionic dye

The PP particles, prepared by Example 4 and untreated *particles* (Reference Example 4) *2* were immersed in a 10% aqueous solution of C.I. Direct Blue 199 dye ~~as the~~ anionic dye *2* and then washed with pure water and dried *2* to observe the washed conditions.

b) Results of evaluation of the surface modification of the PP particles

The following results were obtained by the evaluation tests by immersion in an aqueous solution of *an*

anionic dye.

The PP particles prepared by Example 5 remained lightly cyan in color derived from the dye<sub>2</sub> when immersed in a 10% aqueous solution of C.I. Direct Blue 199 dye ~~as the anionic dye~~<sub>2</sub> and then washed with pure water and dried.

By contrast, the untreated PP particles for Reference Example 4 returned back to the original color of white<sub>3</sub> when immersed in a 10% aqueous solution of C.I. Direct Blue 199 dye<sub>2</sub> and then washed with pure water and dried, indicating that the aqueous dye solution was washed off and that ~~it~~<sup>the surface of the particles</sup> was not compatible with the solution.

As described above, the PP particles prepared by Example 5, where ~~it was~~<sup>the particles were</sup> surface-modified with poly(dimethyl siloxane) having <sup>an</sup> amino group as the functional group, remained lightly cyan in color<sub>2</sub> when immersed in the aqueous dye solution and then washed with water, indicating that the amino-modified poly(dimethyl siloxane) attached to the surfaces of the PP particles<sub>2</sub> when the solution containing the amino-modified poly(dimethyl siloxane), acid and alcohol was spread over the surface and dried. In other words, the PP particles were coated with the amino-modified poly(dimethyl siloxane)<sub>2</sub> and surface-modified into the cationic PP particles by the amino group as a cationic group in the amino-modified poly(dimethyl siloxane).

The PP particles, becoming cationic by the surface modification, reacted with the anionic dye in the aqueous anionic dye solution, to be colored.

5 In the evaluation of the surface modification of the PP particles, cyan dye was used as the anionic dye. However, the PP particles can be colored differently depending on the dye used. This example used the PP particles of 2 mm in diameter. However, use of finer PP particles expands their surface area, possibly  
10 improving <sup>the</sup> coloring ratio of the dye on the PP particles and hence producing ~~the~~ brighter particles.

The colored PP particles can be used as the colorant to be dispersed in ink, <sup>these particles</sup> when ~~they~~ are sufficiently fine.

15 In Example 5, amino-modified poly(dimethyl siloxane) having amino group as a cationic functional group was used for modification of the water-repellent PP surface. However, it is considered that the PP surface can be surface-modified to be anionic, when a  
20 functional group other than a cationic <sup>group</sup> ~~one~~, e.g., anionic functional group, is used as the functional substituent for the poly(dimethyl siloxane) section as the skeleton of amino-modified poly(dimethyl siloxane). An anionic functional group may be used together with  
25 an alkali substance as the cleavage catalyst. Thus, it is considered that PP can be surface-modified to have desired properties for specific purposes by changing

the functional substituent for the poly(dimethyl siloxane) section as the skeleton to be utilized for the surface deposition, depending on surface modification purposes.

5

~~Examples 6 and 7~~ *g*

Examples 6 and 7 applied the method of the present invention to a fibrous element of PP fibers for *a* hydrophilicization treatment, in addition to Example 2 for the element of PP/PE fibers. More *specifically* ~~concretely~~, the element of PP fibers was formed into a rectangular parallelepiped, 2 by 2 by 3 cm in size, comprising the PP fibers of 2 deniers in size.

10

Two types of the hydrophilicization treatment solution, each having a composition given in Table 5 or 6, were prepared.

15

[Table 6]

~~Hydrophilicization~~ treatment solution composition *g*

Components	Composition (wt.%)
Polyoxyalkylene-poly(dimethyl siloxane)	0.1
Sulfuric acid	0.0125
Isopropyl alcohol	99.8875



Table 1

Hydrophilicization treatment solution composition

Components	Composition (wt.%)
Polyoxyalkylene-poly(dimethyl siloxane)	0.1
Sulfuric acid	0.0125
Isopropyl alcohol	40.0
pure water	59.8875

The second composition (for Example 7) was prepared by adding <sup>specific</sup> ~~given~~ quantities of isopropyl alcohol and pure water, in this order, to the treatment solution for Example 2, to <sup>obtain</sup> ~~have~~ the above composition.

This solution also contained sulfuric acid and polyoxyalkylene-poly(dimethyl siloxane) diluted 4 times.

The fibrous elements of PP fibers were hydrophilicization <sup>also</sup> ~~treated~~ <sub>in</sub> in a manner similar to that for Example 2 for the fibrous element of PP/PE fibers, with the solution of the first composition containing isopropyl alcohol as the major solvent (Example 6) and with the solution of the second composition (Example 7).

(Reference Example 5)

The untreated fibrous element of PP/PE fibers was used for Reference Example 5.

The fibrous element of PP/PE fibers for Reference Example 5, having water-repellent surfaces, was

surface-modified to <sup>obtain</sup> ~~have~~ hydrophilic surfaces both by  
Examples 5 and 7, as was the case with the <sup>element</sup> ~~one~~ treated  
by Example 2. In order to evaluate extent of  
hydrophilicity, <sup>properties</sup> the fibrous elements <sup>of</sup> ~~for~~ Examples 6, and  
5 7 and Reference Example 5 were slowly placed on 7 g of  
an aqueous ink solution (surface energy: 46 dyn/cm)  
held by a petri dish.

The untreated fibrous element of PP/PE fibers for  
Reference Example 5 was observed to float on the  
10 aqueous ink. By contrast, those for Examples 5 and 6  
absorbed the ink from their bottom surfaces, <sup>However, the absorption</sup> to clearly <sup>proceeded</sup>  
different extents, <sup>2</sup> ~~however~~. The fibrous element for  
Example 7 totally <sup>absorbed</sup> ~~adsorbed~~ the ink in the petri dish,  
whereas the one for Example 6 <sup>absorbed</sup> ~~almost~~ the half. <sup>The ink</sup>

15 There was no significant difference between <sup>the</sup>  
quantity of polyoxyalkylene-poly(dimethyl siloxane)  
coating the fibrous elements for Examples 6 and 7. The  
difference between these elements in ink-absorbing  
capacity conceivably resulted from <sup>the</sup> difference in <sup>the</sup> extent  
20 of <sup>the</sup> orientation of the polymer itself.

For example, the polymer coating the PE/PP fibrous  
element for Example <sup>while</sup> ~~5~~ was generally oriented, but ~~was~~  
partially disordered. Orientation of the polymer on  
the element for Example <sup>however,</sup> 7 was disordered to a much  
25 smaller extent.

It is considered that the hydrophilicization  
treatment with polyoxyalkylene-poly(dimethyl siloxane)

gives a denser, better oriented coating layer<sup>2</sup> when the treatment solution contains a solvent added to water<sup>2</sup> in addition to isopropyl alcohol. The treatment solution preferably contains at least around 20% of isopropyl alcohol for uniformly wetting the surface. However, the surface may be well coated with a solution containing isopropyl alcohol at below 40% (content of 40% is the level for the solution used in Example 7). Isopropyl alcohol is evaporated faster than other solution components during the solvent evaporation/drying step, <sup>more rapidly</sup> decreasing in content faster. When this phenomenon is taken into consideration, the surface can be coated well with a solution containing isopropyl alcohol at below 40%. Moreover, isopropyl alcohol content of below 40% is preferable from <sup>the viewpoint of</sup> industrial safety.

This invention provides an innovative surface modification method capable of performing <sup>a</sup> desired surface modification based on the new mechanism, which <sup>do not use</sup> ~~uses no~~ ozone, ultraviolet ray or the like for <sup>forming free</sup> radicals ~~formation~~ to process an element for improved properties, nor depends on <sup>a</sup> primer coating (e.g., coating of a silane coupling agent), which may ~~cause~~ <sup>be</sup> uneven ~~coating~~. This invention also provides a treatment solution for the surface modification method, <sup>the</sup> element produced by the method, and <sup>the</sup> surface structure itself obtained by the surface modification.

In particular, the surface modification method of the present invention tries to give an element surface desired functions and/or characteristics of the surface-modifying polymer by orienting the functional group contained in the polymer at the molecular level. It can effectively modify an element <sup>with</sup> ~~of~~ complex surfaces, e.g., <sup>an</sup> ~~A~~ element's inner wall surfaces of complex shapes having hollows or voids. Modification by orientation at the molecular level can greatly reduce a required quantity of the modifier. For example, the present invention can uniformly and continuously <sup>ally treat</sup> ~~hydrophilicize~~ surfaces of polyolefin-based resins finding wide use, e.g., polyethylene and polypropylene.

# ABSTRACT OF THE DISCLOSURE

A surface reforming method capable of efficiently carrying out a sustainable <sup>even</sup> reforming treatment ~~evenly~~ on a prescribed surface part of an element, a surface treatment liquid to be employed for the above-described method, and an element having a reformed surface treated by the above-described method. <sup>Apart of the</sup> ~~The~~ surface of an element ~~to be reformed composing at least a part of the surface of a prescribed element~~ is subjected to the reforming treatment by providing the object surface with a polymer, which is different from a constituent material of the object surface and comprises a first part having a functional group and a second part having an interfacial energy different from that of the functional group and approximately equal to the surface energy of the object surface and orienting the second part of the ~~above described~~ polymer toward the object surface and orienting the first part in the ~~same~~ <sup>a direction</sup> different from the object surface.